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Development and application of a computer simulation tool for ecological risk assessments

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ABSTRACT

DEVELOPMENT AND APPLICATION OF A COMPUTER SIMULATION TOOL FOR ECOLOGICAL RISK ASSESSMENTS

by
Haiyi Lu

In an effort to improve tools in ecological risk assessment (ERA), an ERA software tool was developed and applied. Based on a preliminary evaluation of existing ecorisk models, the relative deficiencies were identified and included the need for a user-friendly interface, an interactive database management system (DBMS), and a comprehensive evaluation of exposure pathways. In this research, Visual Basic (VB) 6.0 and Microsoft SQL server were selected for developing the Windows-based interface and local DBMS, respectively. For the exposure estimate, Yuma and Aberdeen Proving Grounds were identified as baseline ecosystems. Terrestrial and aquatic plant and animal receptor selection was based on the U.S. EPA Guidelines for ERA. All potential exposure pathways were included. Overall, results of the case study of replacing electroplated chromium coatings with sputtered tantalum showed that the most significant exposure resulted from molybdenum and hexavalent chromium, which posed moderately high and slight potential adverse risks to aquatic and terrestrial species at both sites. On the other hand, tantalum (with vanadium as the surrogate) resulted in the least risk to the receptors within the studied areas. However, a slight potential adverse risk was also observed for a large faction of terrestrial mammals at both sites as a result of using sodium vanadate as surrogate for Ta. An uncertainty analysis was included to address the data quality and demonstrated that distribution coefficients have the most influence on the results.

DEVELOPMENT AND APPLICATION OF A COMPUTER SIMULATION TOOL FOR ECOLOGICAL RISK ASSESSMENTS

by
Haiyi Lu

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This thesis is dedicated to
my beloved family.

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CHAPTER 1

INTRODUCTION

1.1 Objective

As part of the Department of Defense "Sustainable Green Manufacturing" initiative, an ecological risk assessment was undertaken to assess the implications of replacing chromium plating with tantalum coatings in artillery gun barrels. In an effort to improve tools in ecological risk assessment (ERA), a comprehensive ERA model was developed based on the case study. With a preliminary evaluation of existing ecorisk models, the relative deficiencies were identified and included the need for a user-friendly interface, an interactive database management system (DBMS), and a comprehensive evaluation of exposure pathways. The developed ERA model includes these features and can be modified for other site-specific applications. Yuma and Aberdeen Proving Grounds were identified as baseline ecosystems and related terrestrial and aquatic receptors were selected based on the U.S. EPA Guidelines for Ecological Risk Assessment. Potential exposure of ecosystem to the gun coatings such as chromium can be a significant adverse impact to the receptors. In this research, the potential risks associated with chromium, tantalum and molybdenum for these two default site conditions were characterized and an evaluation of the model was conducted based on the case study results.

1.2 Overview

An ecological risk assessment process requires a dynamic model that can adapt to specific environmental conditions. In order to build such a model, ecosystem data are required and based on guidance these have been compiled for the two baseline sites,

Yuma Proving Ground (YPG) and Aberdeen Proving Ground (APG) presented in Chapter 2. The associated site-specific characteristics needed include site history, topography, climate, surface water, soil, geology, and groundwater. As part of the ecosystem characterization, concerned terrestrial and aquatic receptors were selected for both sites. The ERA model development is discussed in Chapter 3 where potential exposure pathways include ingestion, inhalation, and dermal absorption for terrestrial animals; root and foliar uptake for plants; and direct absorption for aquatic species. The ERA code has been integrated into the VB interface which is linked to the DBMS. The potential risks associated with chromium and tantalum for the two default sites conditions were subsequently characterized using the model, and the results are presented in Chapter 4. In addition, an overall evaluation of the software is presented with respect to how this code addresses limitations of other models and what deficiencies exist and will be tackled in future work. The last chapter reviews the conclusions from this research and recommendations for the future work.

CHAPTER 2

SITE DATA IDENTIFICATION

2.1 Introduction

In this chapter, the needs of ecosystem data and guidance are presented for the two military sites selected as default ones for the assessment: Yuma Proving Ground (YPG) in Arizona and Aberdeen Proving Ground (APG) in Maryland. Based on U.S. EPA Guidance (U.S. EPA, 1998), the required data include site-specific background and characteristics such as climate, soils, geology, hydrology, and a complete listing of potential animal and plant receptors. Subsequently, the impact of the chemical and physical stressors on these ecosystems are evaluated in the improved dynamic, ecological risk assessment model.

2.2 Guidance for Ecological Risk Assessment

Ecological risk assessment is used to systematically evaluate and organize data, information, assumptions, and uncertainties in order to help understand and predict the relationships between stressors and ecological effects in a way that is useful for environmental decision-making. An assessment may involve chemical, physical or biological stressors and one stressor or many stressors may be considered.

Based on U.S. EPA Guidelines for Ecological Risk Assessment (U.S. EPA, 1998), ERAs include three primary phases: problem formulation, analysis, and risk characterization. The objective of problem formulation is to develop a conceptual model that identifies assessment endpoints (i.e., animal and plant receptors in the ecosystem), data needs (i.e., aquatic and terrestrial toxicity data, site characteristics), and analysis for

characterizing exposure to the system stressors (Hoffman et al., 1995). The final component, risk characterization, tests the conceptual model with toxicity benchmarks resulting in a ranking of the stressor (Hoffman et al., 1995).

The material discussed in this section falls within the first phase, problem formation. This first phase is a process for generating and evaluating preliminary hypotheses about why ecological effects have occurred, or may occur, from human activities. It provides the foundation for the entire ERA. Early in problem formulation, the following questions must be addressed:

- What is the scale of the risk assessment?
- What are the major stressors of concern?
- What are the critical ecosystem and stressor characteristics?
- What is the nature of the problem: past, present, future?
- What data and data analyses are available and appropriate?
- What are the potential constraints (e.g., limits on expertise, time, availability of methods and data)?

Based on these questions, information (actual, inferred, or estimated) is gathered and synthesized on background information, site characteristics, and other associated data, which provide the foundation for developing the problem formulation. Federal and state agencies are recommended for such use; in this work, data were obtained from the following departments and organizations:

- U.S. Environmental Protection Agency (U.S. EPA)
- U.S. Department of the Interior
- U.S. Department of Defense

- U. S. Department of Energy
  - U.S. Fish and Wildlife Service
  - Arizona Fish and Game Department
  - U.S. Geological Survey (USGS)
  - U. S. Army Yuma Proving Ground, Environmental Division
  - U.S. Army Garrison Aberdeen Proving Ground, Environmental Conservation & Restoration Division
  - U.S. Department of Agriculture, Soil Conservation Service
  - Maryland Department of the Environment
  - Maryland Department of Natural Resources
  - Arizona Department of Environmental Quality
  - Arizona Geological Survey

Background information provides general knowledge related to the risk assessment (i.e., the characteristics of the stressors) and assists in identifying the scale and nature of the problem as well as toxicity data needed in the model. Site characteristics cover information about climate, surface water, soil, geology, groundwater, and the ecosystem habitat from which model parameters are generated. However, these parameters can be modified by the user to site-specific characteristics in the code. The code will include the following categories for the parameters: contaminant zone data, cover and contaminated zone hydrological data, saturated zone hydrological data, unsaturated strata hydrological data, and partitioning coefficients. As the code is applied to other ecosystems, site-characteristics should be reviewed thoroughly so that the code parameters can be modified accordingly.

Based on the literature, assessment endpoints are defined; these endpoints are explicit expressions of the actual environmental value that is to be protected, operationally defined by an ecological entity and its attributes (U. S. EPA, 1998). In order to determine how to select and define the endpoints among a broad array of possibilities, detailed information is needed on stressor sources and characteristics, exposure opportunities, characteristics of the ecosystems potentially at risk, and ecological effects. The following subjects and questions (U. S. EPA, 1998) must be considered during the review of this information:

Source and Stressor Characteristics

- What is the source, and is it anthropogenic, natural, point, or diffuse nonpoint?
- What is the type of stressor?
- What is the intensity of the stressor (i.e., the dose or concentration of a chemical)?
- How does the stressor act on organisms or ecosystem function?

Exposure Characteristics

- With what frequency dose a stressor event occur (i.e., is it isolated, episodic, or continuous)?
- What is the duration and how long does it persist in the environment?
- What is the spatial scale of exposure -- the extent or influence of the stressor local, regional, global, habitat specific, or ecosystem wide?

- What is the distribution? How does the stressor move through the environment (i.e., chemical fate and transport; physical movement; biological or the life-history characteristics)?

Ecosystem Potentially at Risk

- What are the geographic boundaries?
- What are the key abiotic factors influencing the ecosystem (i.e., climatic factors, geology, hydrology, soil type, water quality)?
- What are the structural characteristics of the ecosystem (i.e., species number and abundance, trophic relationships)?
- What habitats are present?
- How do the site characteristics influence the susceptibility (sensitivity and likelihood of exposure) of the ecosystem to the stressor(s)?
- What is the landscape context within which the ecosystem occurs?

Ecological Effects

- Given the nature of the stressor, which effects are expected to be elicited by the stressor?
- Under what circumstances will effects occur?

Based on these information, endpoints for ERA should be established. Clearly defined endpoints provide direction and boundaries for the risk assessment and can minimize miscommunication and reduce uncertainty; where they are poorly defined, inappropriate, or at the incorrect scale, the endpoints may be very problematic. Endpoints may be too broad, vague, or narrow, or they may be inappropriate for the ecosystem requiring protection. There are two different endpoints: assessment endpoint and

measurement endpoints. Generally, the assessment endpoint identifies the desired achievement; the measurement endpoints link the existing or predicted conditions on the site to the goals expressed by the assessment endpoints (Maughan, 1992). Achievement of the assessment endpoints is determined through measurement endpoints. Population and community level endpoints are generally preferable but they are restricted to specific site conditions and also limited by the availability of well-documented information. Therefore, in most cases, measurement endpoints for individual organisms are applied. However, it can be important indicators of population or even community endpoints, such as endpoints related to the survival, growth, and reproduction of exposed organisms (Maughan, 1992; U.S. EPA, 1993). Various endpoints may be used for predictive assessments, but the final selection is often affected by the availability of toxicity data in the literature and the quality of the data.

The environmental description for an ecological risk assessment is the ecosystem of concern and its susceptible receptors inherent within specific boundaries. Usually, an environmental description is based on a representative site where a potential release may occur. For purposes of this study, criteria are identified to provide the guidance and basis for defining the endpoint receptors. Besides a set of clear criteria, professional judgment and an understanding of the characteristics and function of an ecosystem are also important for the identification of the endpoints. The less information available, the more critical it is to have informed professionals help in the selection.

In this chapter, the endpoint receptors are selected including the terrestrial and aquatic animals and plants based on the data availability, social and ecological significance, and specific site conditions. As the code is applied to other sites, the user

needs to review the specific site conditions thoroughly, or if appropriate, apply the same receptors housed for the default sites potentially using these as surrogates for their receptors. The relation between receptors and the stressors will be described and analyzed in the evaluation phase; these results are integrated in the risk characterization phase and a risk description is generated (see Chapter 4).

2.3 Site Background

Based on site operations and representative ecosystems, Yuma Proving Ground (YPG) and Aberdeen Proving Ground (APG) were selected as the baseline sites for typical arid and coastal environmental conditions.

Aberdeen Proving Ground occupies more than 72,500 acres in Harford County, MD. As the Army's oldest active proving ground, it was established on October 20, 1917, six months after the United States entered World War I. It has since become one of the Army's premier installation, internationally recognized for research and development, test and evaluation, and soldier training.

The U. S. Army Yuma Proving Ground is located near the Arizona-California border, in the southwest part of the western Range Complex, with 838,174 acres in Yuma and La Paz Counties. Yuma Proving Ground has over 50 years experience testing weapon systems of all types and sizes in a desert environment. The proving ground is regarded as the entire infrastructure for fully and realistically testing all weapon systems in the ground combat arena. They offer a large land area (1,300 square miles) and complete ground combat support facilities. Most importantly, the proving ground has the necessary facilities for a wide variety of commodity areas -- artillery, aviation, armor, tactical vehicle, and air delivery (U.S. YPG, 1999). Because most of the gun barrels coated with

sputtered tantalum will be test fired at Yuma, YPG will receive more attention and focus in this assessment.

2.4 Aberdeen Proving Ground

2.4.1 Location

Aberdeen Proving Ground is located in the northeast portion of Maryland on the western shore of the Chesapeake Bay in Harford County, Md. Its northernmost point is marked by the confluence of the Susquehanna River and the Chesapeake Bay. To the south, it is bordered by the Gunpowder River (Figure 1). The installation consists of approximately 79,000 acres of water and landmass characterized by low-lying marshes, flat meadows and woodland, and gently rolling hills of open and wooded areas. The waters of the Chesapeake Bay, Gunpowder and Bush Rivers, as well as numerous creeks and ponds comprise nearly one half of the area owned or leased by the installation. Approximately 103 miles of unprotected shoreline fall within the installation boundaries (U.S. Army Garrison APG, 1998).

The installation comprises two principal areas separated by the Bush River. The northern area is known as the Aberdeen Area where the Aberdeen Test Center is located, and the southern sector, formerly Edgewood Arsenal (established in November, 1917 - as a chemical weapons research, development, and testing facility), is the Edgewood Area. The two areas were administratively combined in 1971.

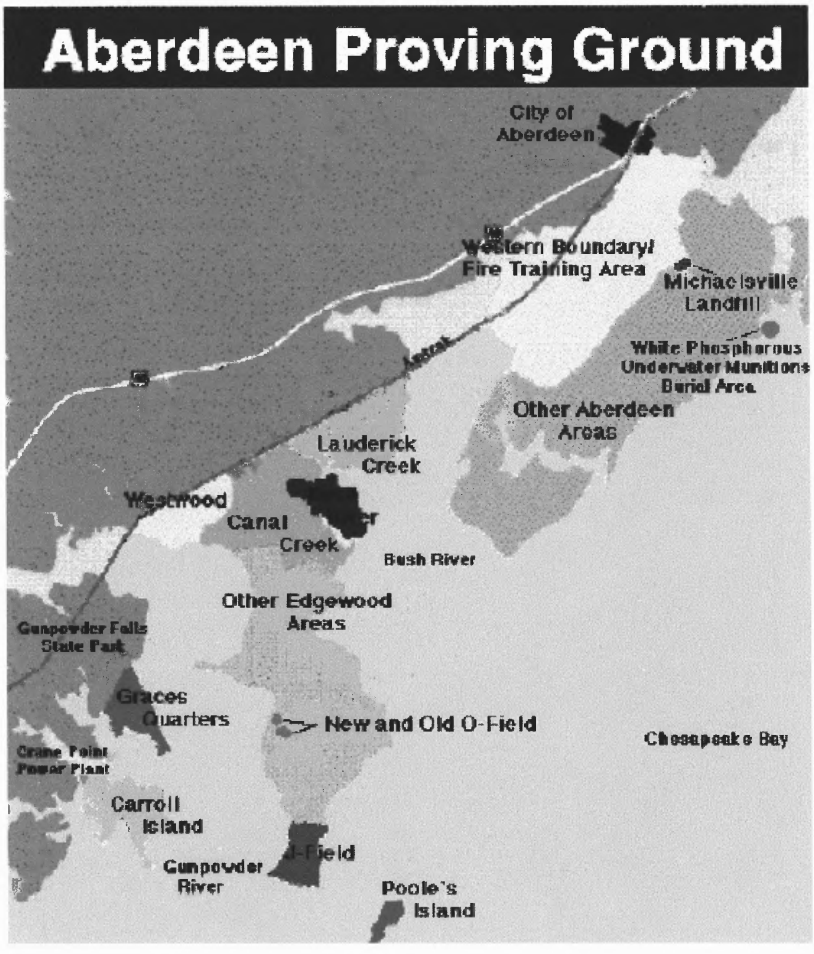

Figure 1 Map of APG Study Areas (U.S. Army APG. 1998)

2.4.2 History

Aberdeen Proving Ground was established on October 20, 1917. Aberdeen's mission included designing and testing ordnance materiel in close proximity to the nation's industrial and shipping centers. The post officially opened on December 14, 1917, and the first gun was fired on January 2, 1918.

Originally, the Aberdeen and Edgewood Areas were two separate facilities. Aberdeen was used as a site for proof of concept and equipment test approval; development has included munitions, firearms, vehicles, aircraft, and protective clothing. The first artillery round was fired at Aberdeen on January 2, 1918. A total of 416,294 rounds were fired at Aberdeen during World War I. Edgewood was developed at the same time to provide chemical production and artillery shell filling facilities to respond to the need for chemical weapons. The main chemicals produced were phosgene, chloropicrin, and mustard gas.

During World War II, Aberdeen became the Ordnance Research Center, a research and development site for new armor, ammunition, rockets, aviation armament, and other equipment. Aberdeen experienced an impressive increase in activity soon after World War II; researchers at Aberdeen produced the world's first computer, Electronic Numerical Integrator and Computer (ENIAC) to assist in research and in refining firing tables (U.S. Army Garrison APG, 1998). Chemical production at Edgewood ceased, and the facility's focus shifted to research and development, especially for chemical weapon defensive measures. In 1971, the Aberdeen and Edgewood facilities were joined to form one administrative unit, Aberdeen Proving Ground.

2.4.3 Topography

Aberdeen Proving Ground is located within the Atlantic Coastal Plain, which is characterized by low-laying wetlands, flat to gently rising knolls and hills, with little change of elevation. These features were created as material eroded from the hills to the West. The topography and surface features are characterized by these low hills, shallow valleys, flat plains, and extensive marshes and wetlands (U.S. Army Garrison APG, 1998). Elevations within the proving ground range from 0-70 feet above sea level. Small creeks drain the land surface erosion and discharge into the Chesapeake Bay or the Bush and Gunpowder Rivers, tributaries of the Bay. The shoreline is typical of the Bay's western shore, from low, marshy shorelines to steep, eroding bluffs 15-20 feet in height.

2.4.4 Climate

Aberdeen Proving Ground lies in the Coastal Plain region of the eastern seaboard of the United States. The climate is influenced by continental and maritime air, which originates over land and water, respectively. It is characteristically warm, temperate, rainy, and moderately humid without a dry season. The mean annual precipitation is 40 inches and is fairly uniformly distributed throughout the year. The heaviest rainfall usually occurs in summer during thunderstorms, which are frequent in the area. Snowfalls occur on average of 25 days each year with amounts in excess of one inch. The heaviest snowfalls are in January, but accumulations may occur as late as March.

The mean annual temperature is 54° Fahrenheit (U.S. Army Garrison APG, 1998). The general flow of the atmospheric currents is from west to east. These tend to bring cold, dry continental air masses into the area. However, the Appalachian Mountains

to the west shelter the area from the severity of the cold continental air masses. The moderating effects of the Atlantic Ocean and Chesapeake Bay combined with the prevailing atmospheric currents tend to produce warmer, milder winters in the area than are experienced by the inland regions at the same latitude. During the summer, the area is influenced by a large semi-permanent high pressure system centered over the Atlantic Ocean near 30 degrees north latitude in the vicinity of Bermuda. The associated flow of warm, moist air from the south contributes to the high temperatures and humidity, and provides moisture for frequent afternoon and evening thunderstorms.

The prevailing winds are from the west to northwest during the winter and south to southwest during the summer. The annual average wind velocity is approximately 10 mph. The highest average wind speeds occur during spring and winter. Occasionally, during thunderstorms, tropical storms, hurricanes, or intense winter storms, the wind can reach velocities in excess of 50 mph.

2.4.5 Surface Water

Aberdeen Proving Ground is within the Upper Chesapeake Subregion of the Mid-Atlantic Region. The Upper Chesapeake Subregion has a drainage area of approximately 7,400 $mile^2$ in Maryland. This area comprises the major part of the Coastal Plain in Maryland and one-third of the Piedmont province. Principal rivers in the subregion include the Patuxent, Patapsco, Gunpowder, Chester, Choptank, Nanticoke, and Pocomoke. Major storage is provided by Liberty Reservoir on the Patapsco River (completed in 1954 with 129,000 acre-ft or 42,100 Mgal of storage), and Prettyboy (completed in 1933) and Loch

Raven (completed in 1914) Reservoirs on Gunpowder Falls with a combined storage capacity of 133,000 acre-ft or 43,300 Mgal (James, 1997).

The Gunpowder is in the upper western shore of Chesapeake Bay. It covers most areas of the APG and is one of the main surface water resources of this area. The dissolved oxygen (DO), water temperature, and pH of the Gunpowder are illustrated in Figures 2-4, and the data were collected from the GUN0125 station by Maryland Department of Natural Resource's (MD DNR) Tidewater Ecosystem Assessment Division (MD DNR, 2000). The water temperature changes with seasons: the highest and lowest ones occur in July and January, respectively (Figure 2). The change of temperature also influences the DO concentrations at the greatest depths; generally, during summer, the DO concentration decreases and reaches a minimum in July. On the other hand, as temperature decreases, DO concentration increases and peaks in January (Figure 3). Compared with the temperature and DO, the pH of the Gunpowder does not vary and is typically 7.5 (Figure 4).

Runoff varies geographically and seasonally, depending on the geology and the seasonal precipitation patterns. During the winter months of December through February, precipitation falls primarily as snow, and runoff rates are relatively low. During the spring months of March through April, snowmelt and rain saturate soils and along with reduced evapotranspiration increase runoff. On the other hand, runoff during the summer months of June through September is low because of large evapotranspiration losses. During October and November, runoff increases as evapotranspiration declines at the end of the growing season.

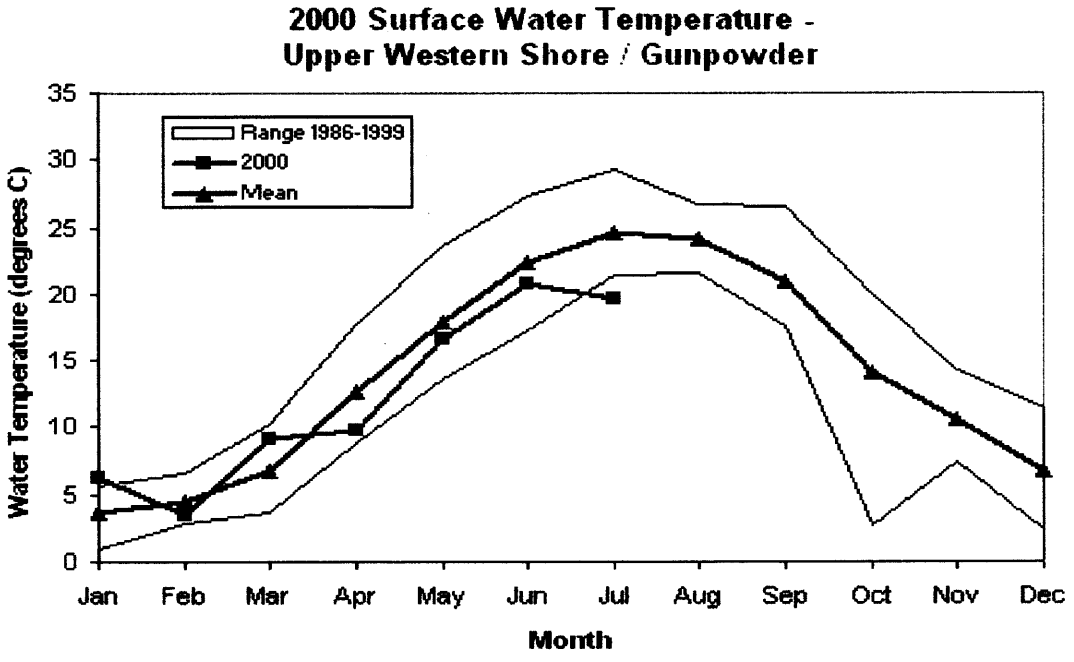

Figure 2 Gunpowder River - Water Temperature (Measuring Station: GUN0125) (MD DNR's Tidewater Ecosystem Assessment Division, 2000.)

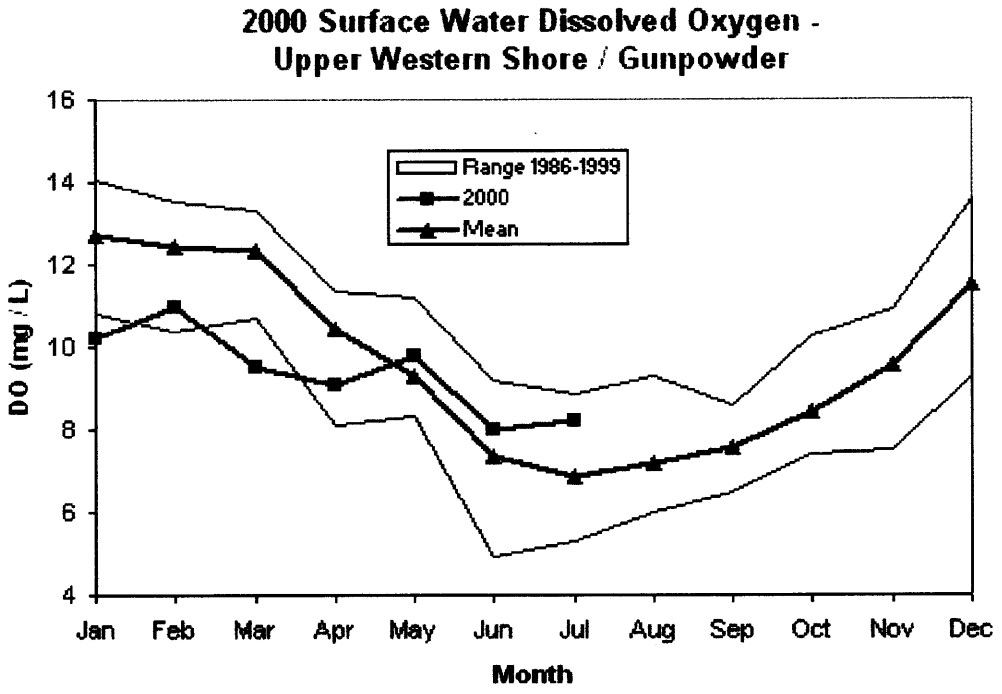

Figure 3 Gunpowder River - Dissolved Oxygen (Measuring Station: GUN0125) (MD DNR's Tidewater Ecosystem Assessment Division, 2000.)

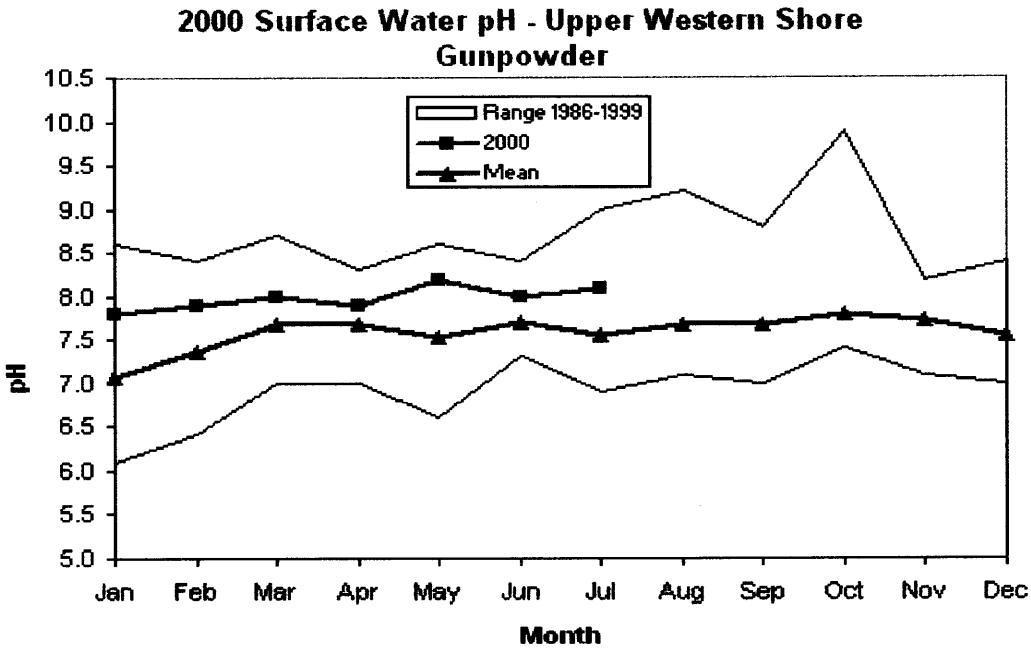

Figure 4 Gunpowder River – pH (Measuring Station: GUN0125) (MD DNR's Tidewater Ecosystem Assessment Division, 1999)

2.4.6 Soil

Aberdeen Proving Ground's soils are deep, nearly level to steep, moderately to well drained, and are underlain by sandy, loamy, gravelly, or clayey sediments on smooth uplands. Soils of the floodplains and low terraces are generally deep, nearly level, moderately well drained to well drained, and are underlain by stratified alluvial sediments. The dominant soils at the proving ground are the Sassafras, Elkton, and Keyport series. All three series developed from the deposition of marine sediment. Along most nontidal wetland areas, the Meadow series/Alluvial land series is dominant. In tidal influenced wetlands, the Tidal Marsh series is dominant (U.S. Army Garrison APG, 1998.).

2.4.7 Geology

The Atlantic Coastal Plain at APG consists of deep layers of unconsolidated sediments. These sediments include mixed layers of clays, silts, and sands with occasional gravel lenses (bowl shaped formations). The sediments are underlain by crystalline igneous and metamorphic rocks from the Precambrian to lower Paleozoic era. Schist, gneiss, gabbro, granites, marble, and quartzite are some of the minerals found in this area. The northern end of APG lies near a fault line, which marks the boundary between the Atlantic Coastal Plain and the Appalachian Piedmont region. Sediment layers in this area are approximately 200 feet deep. At the southern end of APG, Coastal Plain sediments thicken to a depth of more than 900 ft (McGreevy et al., 1985).

The youngest sediments within the Coastal Plain were deposited in the Quaternary or Pleistocene Series, which is dominated by the Talbot Formation,

approximately 1 million years old. These are layers found in the bay and estuaries where eroded material has been deposited. Next in the series is the Tertiary Formation, which is mainly comprised of the Pliocene Formations from 2-5 million years ago. These sediments were deposited during periods of changing sea level. The oldest type of sediment is the Cretaceous Formations, which were formed 70-130 million years ago and principally composed of the Potomac Group (McGreevy et al., 1985). These sediments were deposited when the Atlantic Ocean was just beginning to form. The accumulation of sediment resulted in the Coastal Plain (Figure 5).

2.4.8 Ground Water

Ground water is an abundant natural resource in this area. Aberdeen Proving Ground is located in the Coastal Plain where the aquifers are characterized as unconsolidated ones. Specifically, these consist for the most part of the Columbia and Potomac Groups (Figure 5) (McGreevy et al., 1985). The unconsolidated deposits underlying the Coastal Plain form a thickening sequence that consists of sand and gravel aquifers interlayered with silt and clay confining beds. These deposits are underlain by consolidated rock similar to that of the Piedmont, at depths ranging from the surface at the Fault Line to about 8,000 feet at Ocean City (McGreevy et al., 1985). With the exception of the Columbia aquifer, the Coastal Plain aquifers generally are confined except where exposed or overlain only by permeable surficial sediments.

The Columbia aquifer, which is the uppermost hydrogeologic unit of the Coastal Plain in most of Maryland, is used as a principal drinking water supply throughout that area. The aquifer generally is unconfined, but deeper zones are confined locally by clay

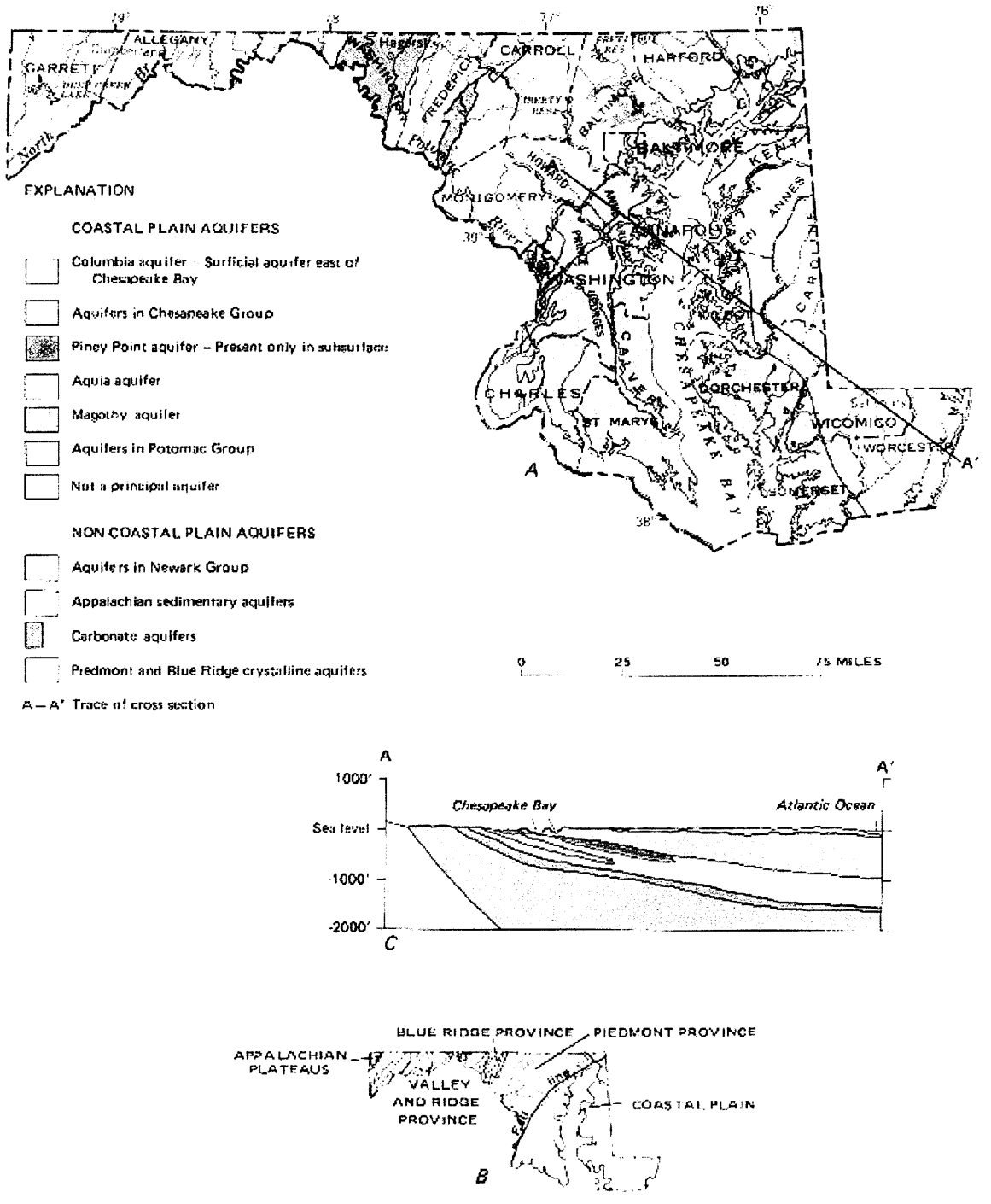

Figure 5 Principal Aquifers in Maryland and the District of Columbia. A, Geographic distribution. B, Physiographic and division. C, Generalized cross section (McGreevy, et al., 1985)

lenses. Well yields of Coastal Plain aquifers depend on thickness and intergranular permeability of the sand and gravel layers as well as well construction. Where permeable layers are sufficiently thick, well fields may produce several million gallons per day. Most Coastal Plain aquifers also contain saltwater in deep areas. The USGS has conducted detailed hydrogeologic investigation at several areas within the Edgewood area -- the major area of APG, the Canal Creek area, Graces Quarters, the O-Field area, Carroll Island, and the J-Field area (Figures 6 – 12) (Donnelly et al., 1998). The flow directions marked with "?" in Figure 10-12 are still under study. From these figures, the Chesapeake Bay could potentially be impacted by contaminant transport through groundwater. However, the groundwater flow velocity is low as a result of the low gradient in the APG aquifer, and a high water table is common at APG. These two factors may hinder the contaminants transport in the groundwater.

Natural water quality is generally suitable for most uses; locally, however, excessive concentrations of iron (0.3 milligrams per liter [mg/L]) may exist and the water can be hard (120 mg/L as calcium carbonate) (Hansen, 1972). The water may also be slightly acidic in some areas with pH as low as 5. In a few locations, aquifers have been contaminated from surface sources (Donnelly et al., 1998).

2.4.9 Ecology

Aberdeen Proving Ground provides large areas of natural habitat for many species. The post is composed of roughly 50% hardwood forest, 34% mowed/grassy areas, 13% marsh or marsh shrub, 2% bare earth, and 1% shrub habitat (U.S. Army Garrison APG, 1998).

Forested regions represent a transition zone between the oak-pine and oak-chestnut regions of the eastern United States. APG contains large areas of wetland. These provide habitat for plant species such as the slender blue flag, an endangered marsh plant. Specifics on the animal and plant receptors are discussed in more detail in Section 2.6, Ecosystem Animal and Plant Receptors.

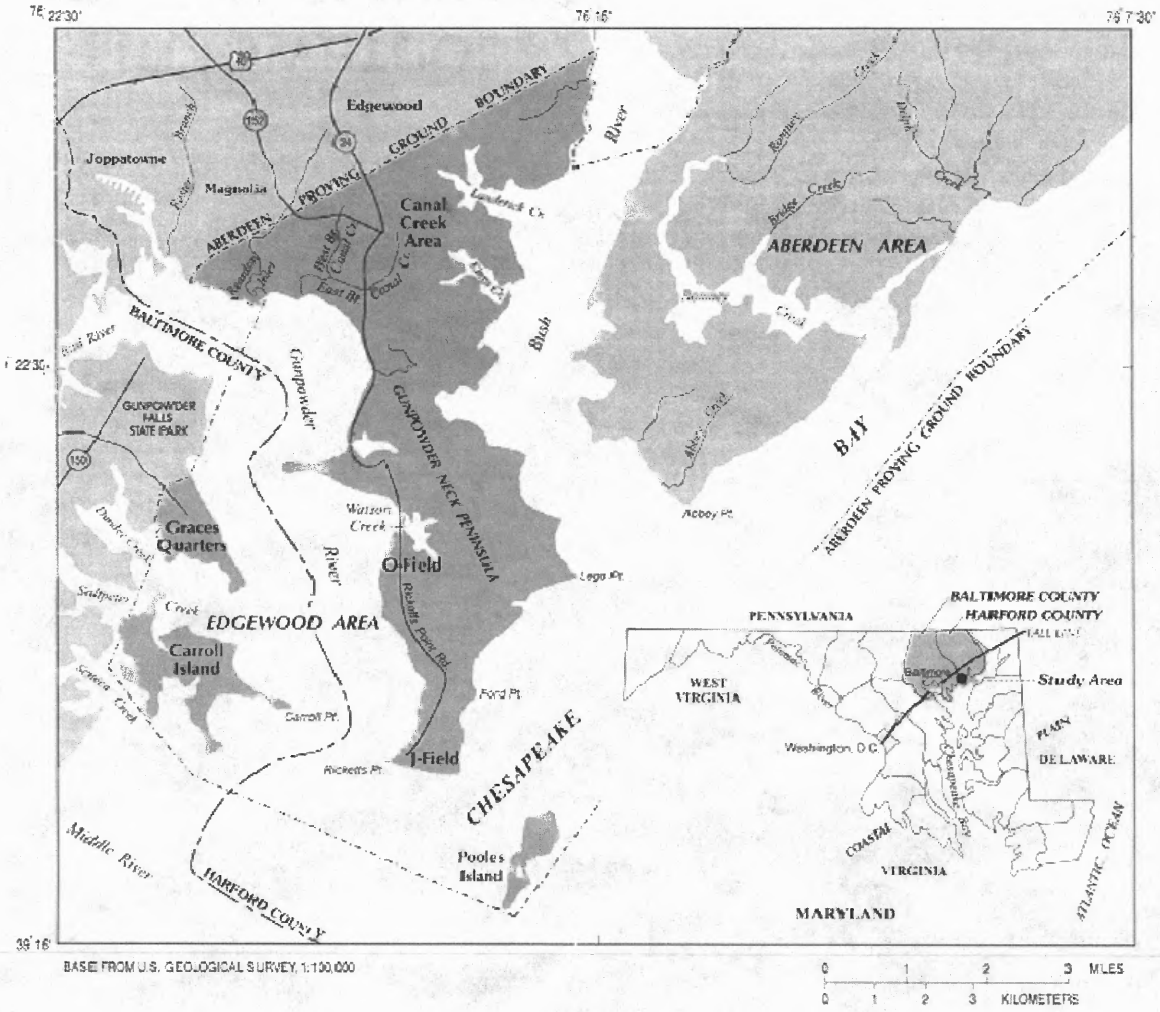

Figure 6 Edgewood Area, APG (Donnelly et al., 1998)

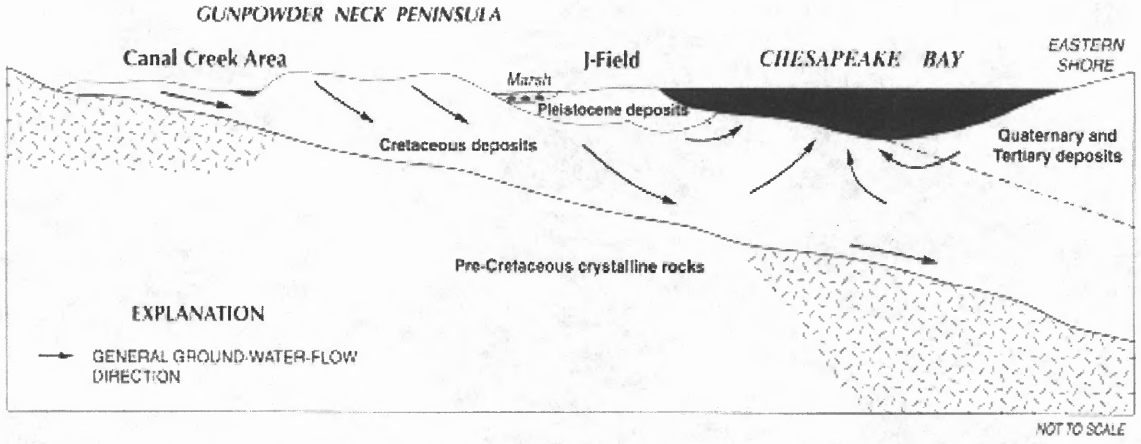

Figure 7 Geological Units and General Ground-water-flow direction in the upper Chesapeake Bay area (Donnelly et al., 1998)

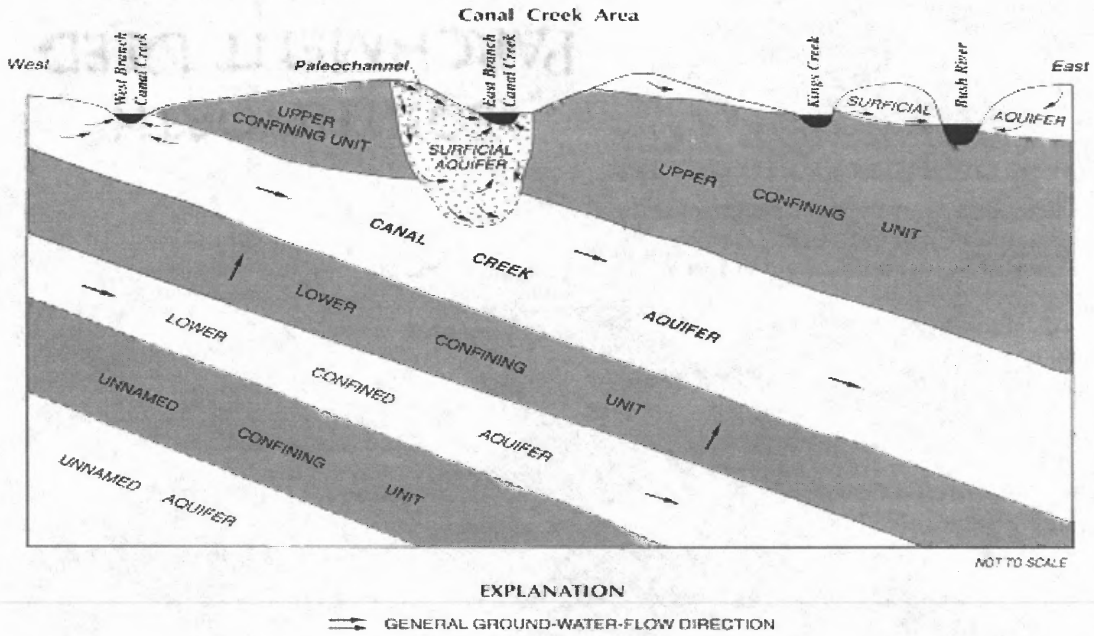

Figure 8 Hydrogeologic Units and General Ground-water-flow Direction in the Canal Creek area (Donnelly et al., 1998)

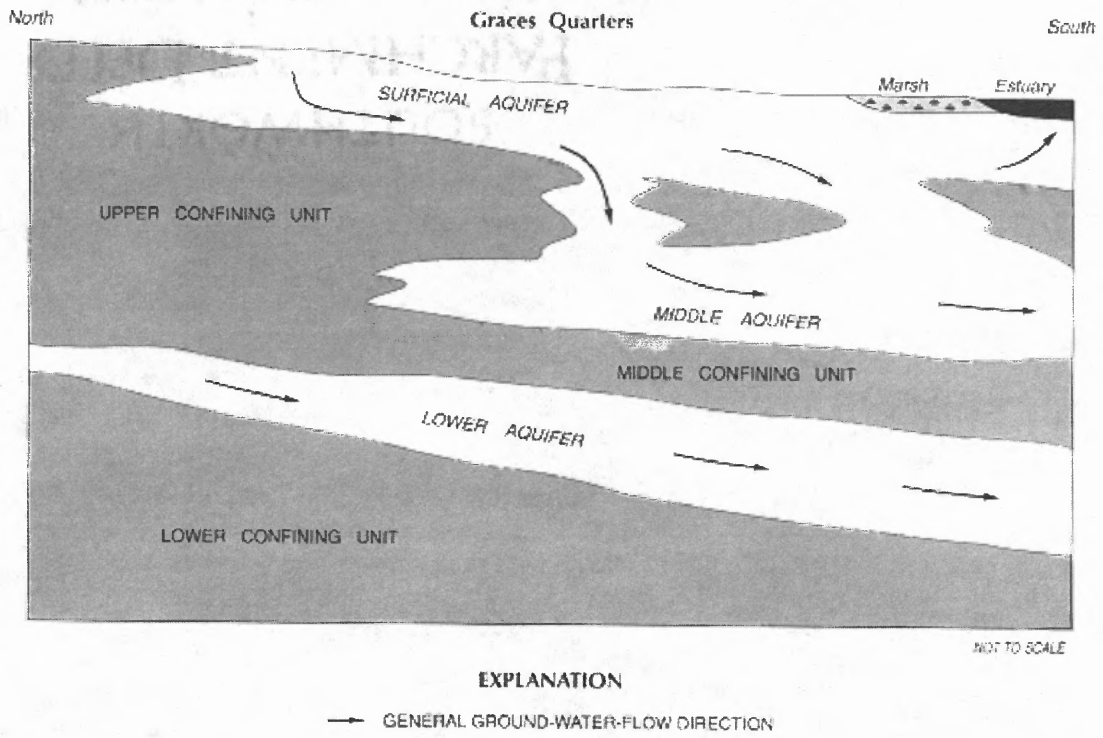

Figure 9 Hydrogeologic Units and General Ground-water-flow Direction at Graces Quarters (Donnelly et al., 1998)

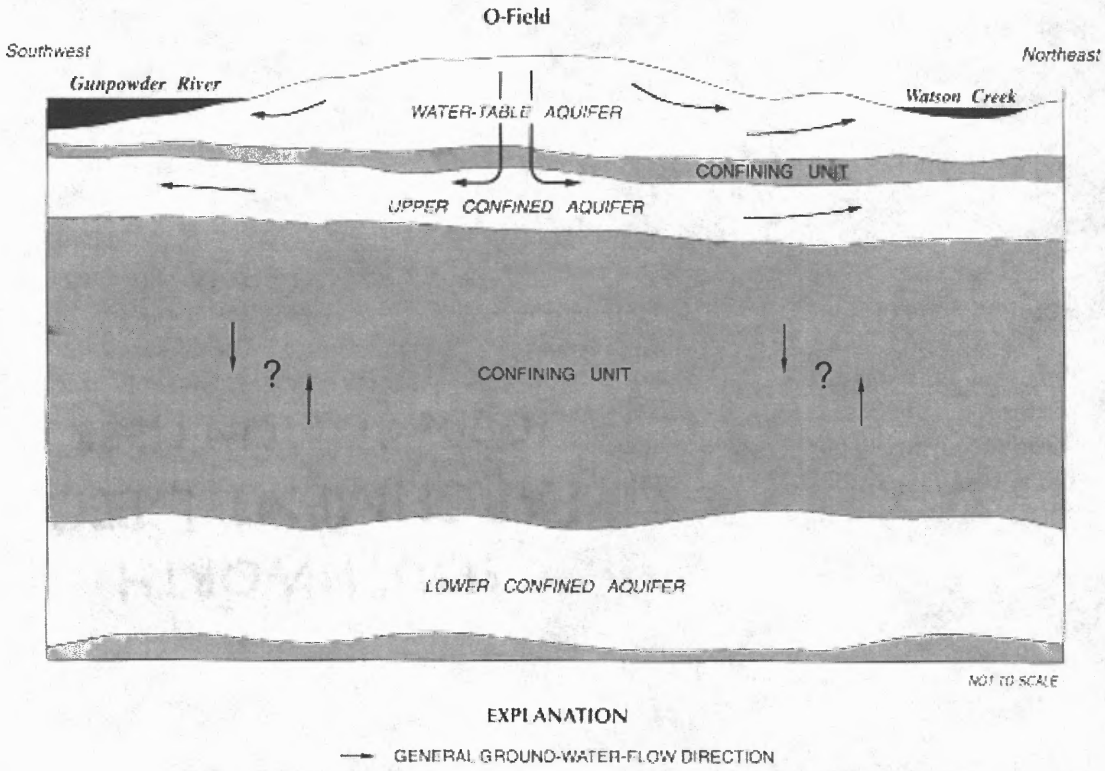

Figure 10 Hydrogeologic Units and General Ground-water-flow Direction in the O-Field Area (Donnelly et al., 1998)

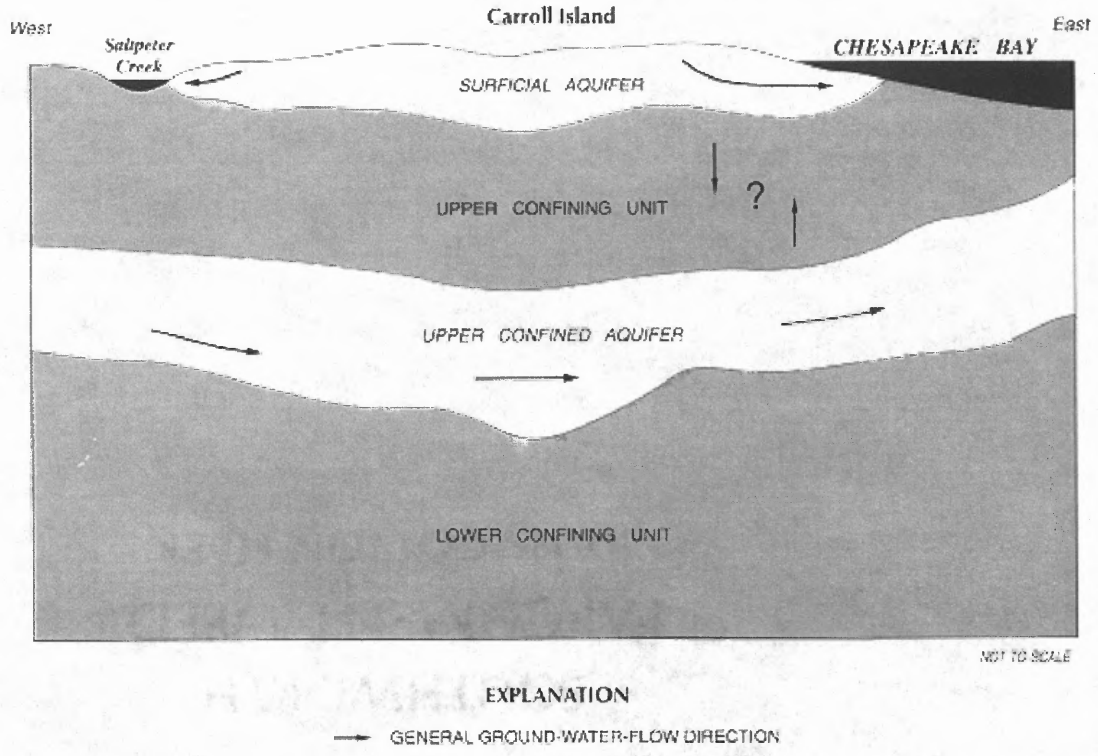

Figure 11 Hydrogeologic Units and General Ground-water-flow Direction on Carroll Island (Donnelly et al., 1998)

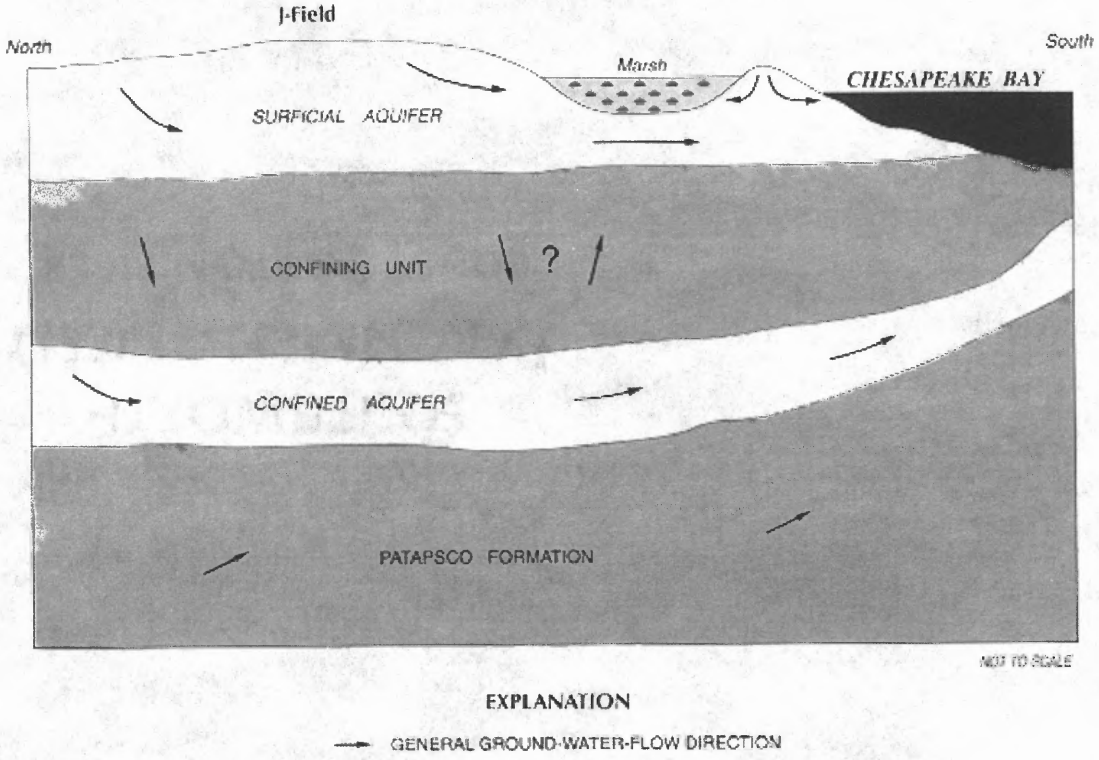

Figure 12 Hydrogeologic Units and General Ground-water-flow Direction in the J-Field Area (Donnelly et al., 1998)

2.5 Yuma Proving Ground

Yuma Proving Ground (YPG) is a vast installation, over 837,000 acres. Closely matching the terrain and weather conditions of the Persian Gulf, many units routinely train here to take advantage of the real-world environment. Yuma Proving Ground conducts tests on medium and long-range artillery, aircraft target acquisition equipment and armament, armored and wheeled vehicles, a variety of munitions, and personnel and supply parachute systems (Figures 13 and 14). Testing programs are conducted for all United States military services, friendly foreign nations, and private industry.

2.5.1 Location and Size

The U.S. Army Yuma Proving Ground is near the Arizona-California border, approximately 26 miles north of the city of Yuma, Arizona. The main area is located in the southwest part of the Western Range Complex. At 1,300 square miles, it has the size necessary to fully exercise army weapon systems without endangering the public, the isolation to avoid encroachment, the climate and vegetation to potentially avoid environmental issues, and the sea level altitude critical for a helicopter test center (Figure 15).

The U.S. Army YPG is in the Sonoran Desert, an area of great similarity in both terrain and climate to the Middle East. For that reason, it's the Army's Desert Environmental Test Center. Yuma Proving Ground holds the distinction of being one of the largest military installations in the world (Figure 15).

Figure 13 Yuma Proving Ground

Figure 14 Cannon Tested in Yuma Proving Ground

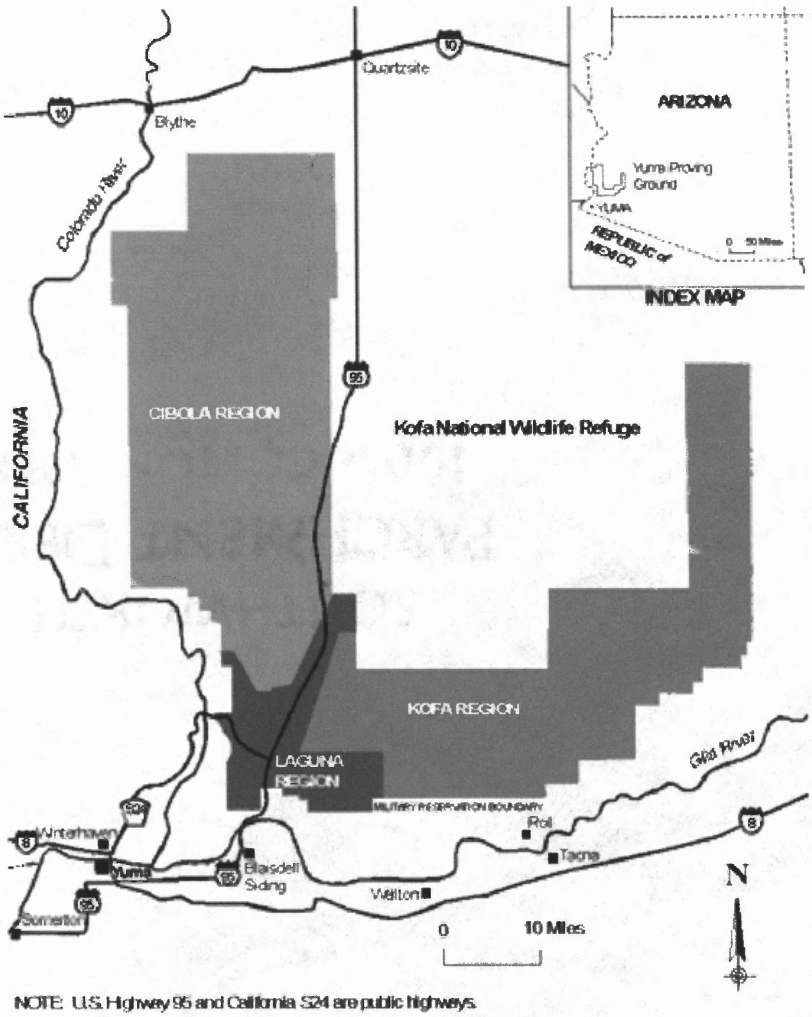

Figure 15 Map of USAYPG Study Area (U.S. Army YPG. 1998)

2.5.2 History

Yuma Proving Ground is a general-purpose facility with over 50 years experience testing weapon systems of all types and sizes. The U.S. Army Corps of Engineers opened the Yuma Test Branch near the present site of YPG in early 1943. Initial office and dormitory buildings were obtained from the Bureau of Reclamation about 1 mile from the test site. Additional facilities were constructed at the Colorado River test site by Italian Prisoners of War who had been captured in North Africa (U.S. Army YPG, 1999).

The first major project undertaken at the test branch was the redesign of a portable steel tread way bridge used by heavy armored vehicles in combat areas (U.S. Army YPG, 1999). Testing continued until the conclusion of the war in 1945. Though work at the test branch declined after the war, it remained operational for several more years. Five years after the war ended, the test branch closed, only to reopen -- with a greatly expanded mission -- in 1951. It is from these beginnings, based on steel bridges and other river-related improvements that the Yuma Proving Ground of today has grown.

The U.S. Army YPG of today features approximately 1,700 military and civilian employees. Employed in a wide variety of occupations, the mission of YPG's workforce is to use advanced technology to carry out sophisticated tests of aircraft armament systems, air delivery systems, tank-automotive equipment, and much more (U.S. Army YPG, 1999). Approximately 100 tests are ongoing at the proving ground at any single time.

2.5.3 Topography

The land area of the Yuma Proving Ground consists of a variety of desert terrain features. Approximately 40% of the total area is covered by rugged, deeply dissected mountains in linear ranges with maximum elevations of 2,822 feet (869 meters). These mountains are predominantly composed of schist, granite, and other rock types. The remaining land areas consist of well-developed alluvial fans and steep-sided washes (Figure 16).

2.5.4 Climate

As mentioned earlier, YPG is located in the Sonoran Desert, a low-elevation, hot, and arid desert. The climate is characterized by clear skies, low relative humidity, slight rainfall, and large daily temperature variations. According to meteorological records, the average daily temperature ranges from 27°C (80°F) to more than 38°C (100°F) during summer months, and from 4.3°C (40°F) to 19°C (65°F) during winter months. The all time record high temperature is 51°C (124°F), which occurred on July 28, 1995. The all-time record low temperature is –5°C (23°F) which occurred on January 8,1971. A 39-year (1954 through 1995) Climatological Summary of YPG (Yuma Meteorological Team, 1996) is shown in Table 1.

The wind speed averages three knots during September through February. From March through August the average wind speed is four to five knots. The windiest time of the year is in the spring and summer with normally more than 10 days per month having wind gusts of over 10.29 meters/second (20 knots) (Woodcock, 1992). The prevailing direction is from the north to northwest from late autumn until early spring. As temperatures warm, winds shift to a more southerly direction. Winds associated

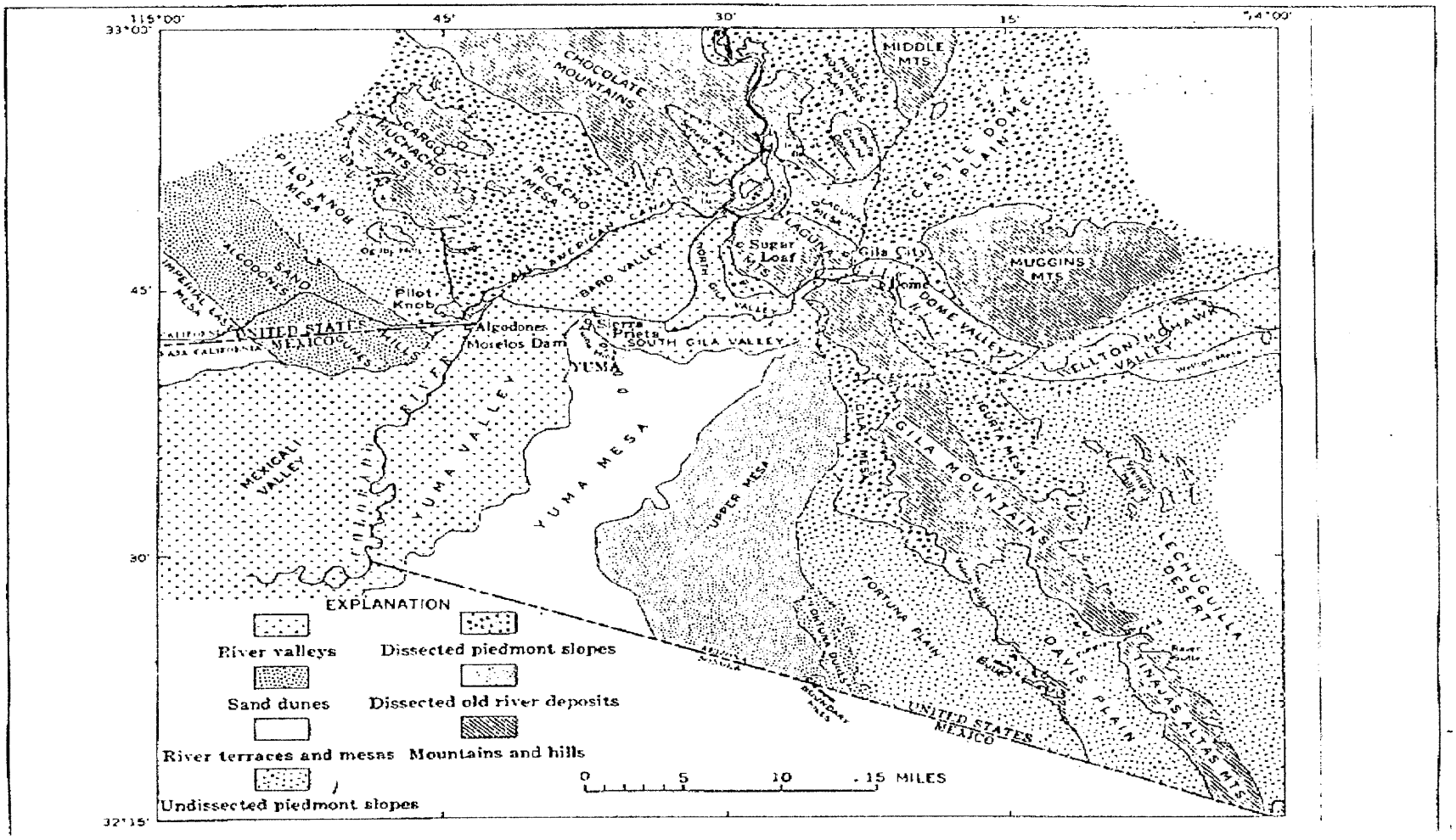

Figure 16 Topography for YPG (Entech Engineers, Inc., 1988)

Table 1 Climatology Summary 1954-1992 (Yuma Meteorological Team, 1996)

	MONTH	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
TMPERATURE (°F)	Extreme max T	89	94	100	106	117	121	118	118	115	112	95	84
	Average max T	67	73	77	85	92	102	106	104	100	89	76	67
	Mean T	54	59	65	71	78	88	93	92	86	75	62	54
	Average mint	42	46	50	56	64	73	80	79	73	61	49	42
	Extreme mint	23	26	32	42	46	54	65	65	54	36	31	25
AVERAGE HUMIDTIES (%)	0500 mountain standard time	55	48	49	36	33	30	42	51	48	44	47	60
	1700 mountain standard time	27	22	20	14	12	10	20	24	21	21	24	33
	Average humidity All hours	42	37	34	24	21	19	30	37	34	33	36	47
PRECIPITATION (inches)	Average precip, INS	.51	.28	.39	.10	.04	.06	.22	.63	.44	.34	.30	.37
	Max. monthly Precip	2.26	1.36	2.50	.65	.26	1.31	1.39	2.55	2.63	3.78	1.73	2.16
WINDS	Average wind speed (knots)	3	3	4	4	5	4	5	4	3	3	3	3
	Prevailing wind Direction	N	N	W	W	W	W	SSW	SW	SW	W	NNW	NNW
	Extreme peak wind (knots)	33	38	45	42	34	29	55	60	50	35	41	45

with the summer monsoons shift toward the southeast (Woodcock, 1992).

2.5.5 Surface Water

There is no permanent surface water at YPG, and only occasionally do the washes carry runoff from rainstorms. During period of intense rainfall, ponding and flash flooding occur. Natural rock tanks occur in the more mountainous regions, but dry out during long periods without rainfall (U.S. Army YPG, 1999).

The Colorado River and Gila River are two major permanent water sources existing outside YPG boundaries. The Colorado River traverses a generally north-south direction to the west of the proving ground. The Gila River traverses east-west south of YPG. Surface water drainage in the central and eastern parts of YPG flow into the Gila River. Infrequent rainfall produces localized flash-flooding and temporary surface water, especially during thunderstorms in August and September, Rainfall averages 3.5 inches (8.9 cm) per year, and the evaporation rate is 107 inches (271.8 cm) per year. The combination of low precipitation and high evaporation prevents surface water from infiltrating deeply into the soil. Thus, most of the year, desert washes are dry, but during heavy rainstorms, these washes drain surface water (Entech Engineers, Inc., 1988). Washes vary in size, from less than a meter in width and depth, to more than a kilometer in width and 10 meters in depth.

Yuma Proving Ground also has few natural year-round sources of water, which occupy a small area at YPG. Some natural water tanks have been modified to provide year-round water to wildlife. Four types of water sites used by wildlife included Tinajia,

Enhanced Tinajia, Water Catchments, and other man-made water sources (Palmer, 1986). Figure 17 illustrates the surface drainage around YPG.

2.5.6 Soil

The lower Sonoran desert environment at YPG is characterized as terrestrial ecosystem, and soil is considered an important transport pathway in the ecological risk assessment. All the soils on the Proving Ground are classified by the Soil Conservation Service, Department of Agriculture, as hyperthermic aridisol (Entech Engineers, 1988). This soil type occurs as a result of an environment that has a mean annual soil temperature of at least 22°C (72°F) with more than 5°C (9°F) difference between mean summer and winter temperatures. This topsoil has a depth of 50 centimeters (20 inches), under which lies bedrock. It also lacks sufficient precipitation to produce crops without irrigation, generally supporting only sparse strands of desert shrubs, a few trees, and perennial grasses.

According to Chamberlin and Richardson (1974), the soils at YPG consist of four series; these are (1) Gilman-Vent-Brios, (2) Harqua-Perryville-Gunsight, (3) Coolidge-Wellton-Antho, and (4) Lomita-Rock Outcrop (Figure 18). Table 2 is a summary of the characteristics and properties of the four series of soil.

Generally, Gilman-Vent-Brios Association soils are found only on the flood plains of the Colorado and Gila Rivers, along the southwest and west portions of the YPG. The soils consist mainly of sandy loam and fine sands. Soils of the Coolidge-Wellton-Antho Association are found northeast of the Laguna Mountains, and in the southwest corner of the YPG. These soils are similar to those the Harqua-Perryville

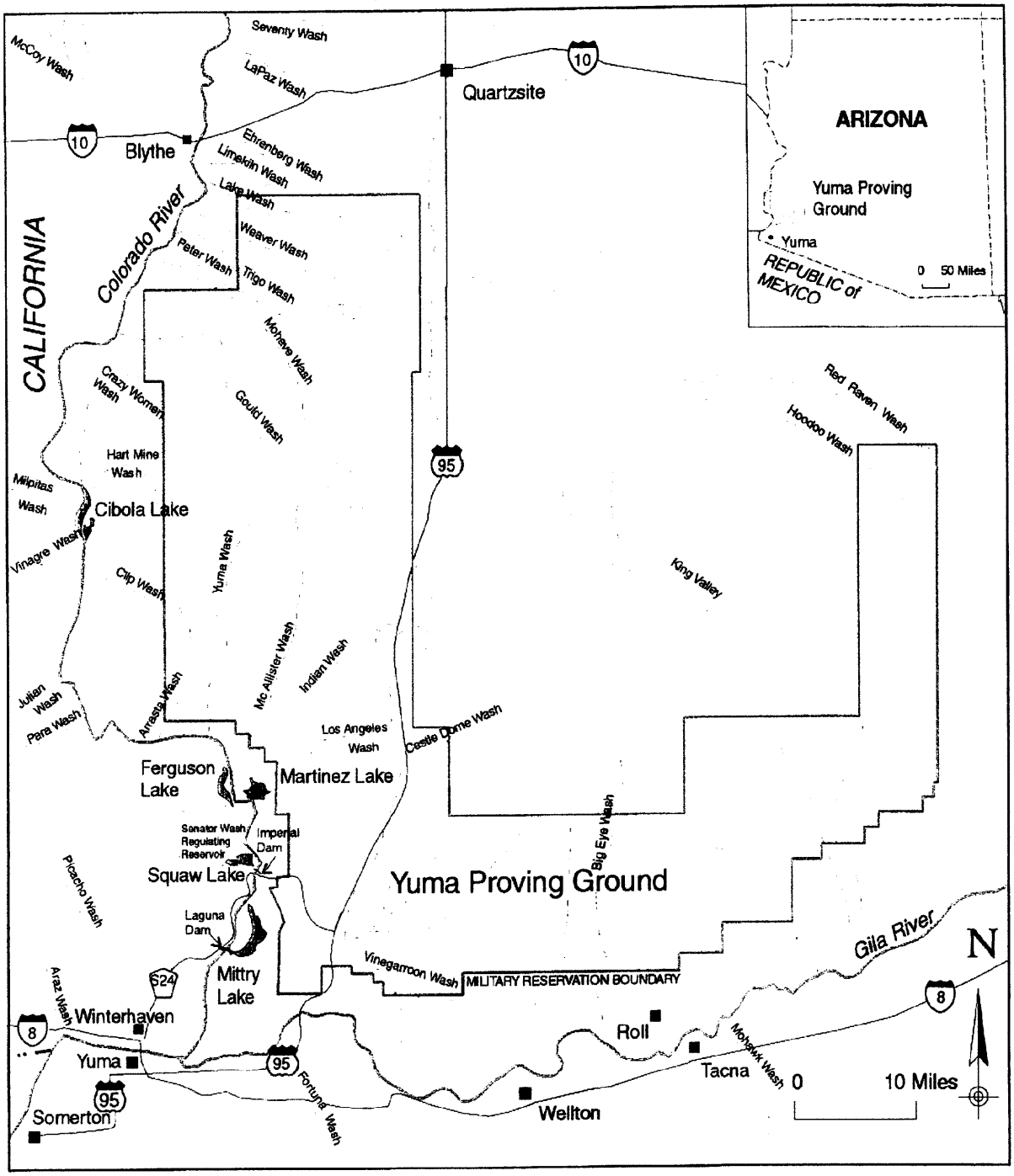

Figure 17 Surface Drainage of YPG (Entech Engineers, Inc., 1988)

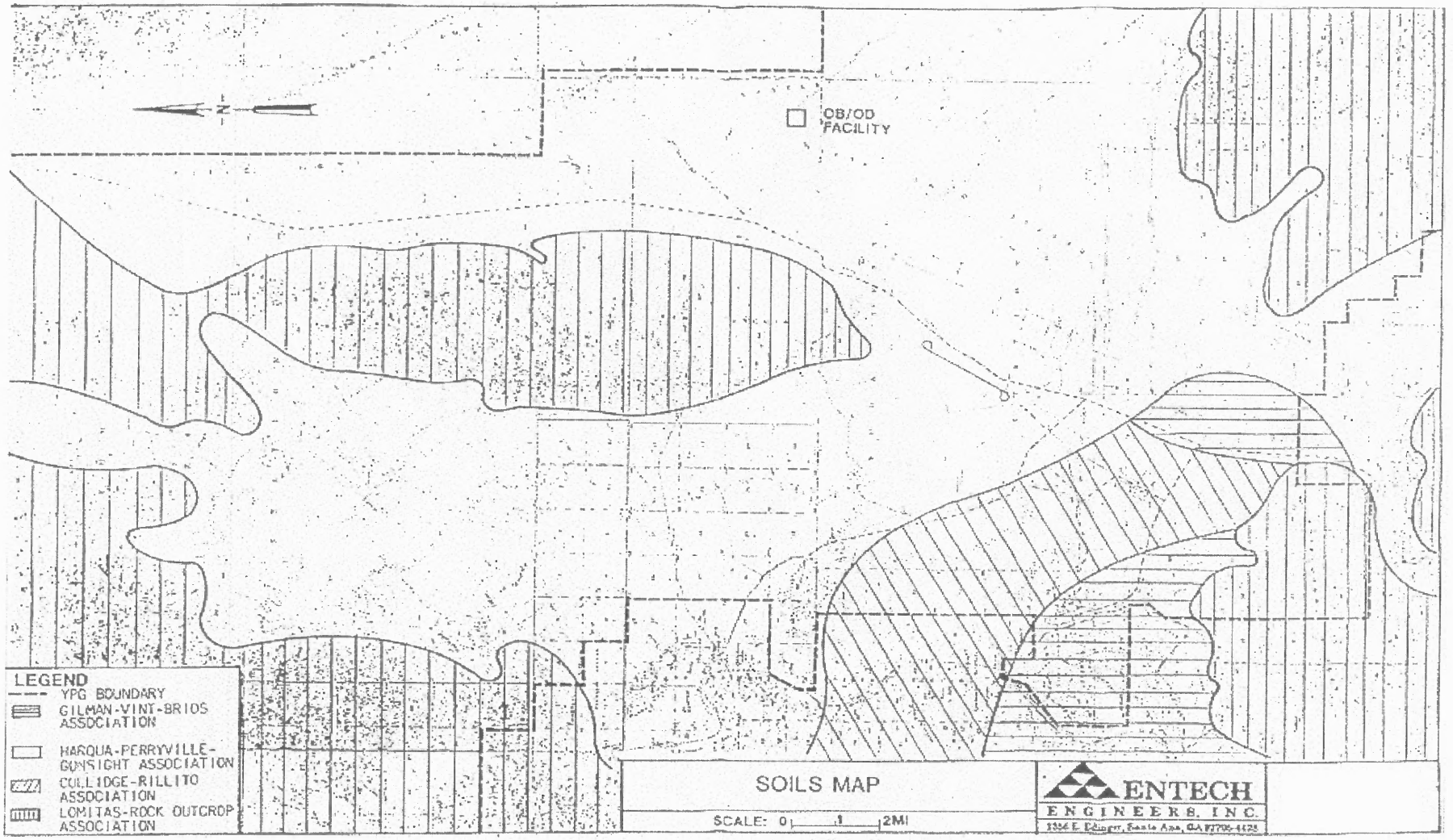

Figure 18 Soil of YPG (Entech Engineers, Inc., 1988)

Table 2 Soil of YPG (Entech Engineers, Inc., 1988)

Series Association and Occurrence[1]	Elev. Range	Thickness	PH[2]	Permeability	Water-holding Capacity	Infiltration Rate	Runoff Potential
Gilman-Vint-Brios. Deep, medium and coarse-textured soils on flood plains; from mixed igneous and sedimentary sources.	305 - 457m	18m	7.4 - 8.4	Moderate to Rapid	High to Low	Moderate	Moderate
Margua-Perryville-Gunsight. Deep, gravely moderately fine and medium-textured soils high in lime concretions, and very gravelly calcareous soils on old alluvial fans: from volcanic and calcareous, some granitic, and sedimentary sources.	91 - 457m	18m	7.4 - 9.4	Moderate to Moderately Slow	Moderate to Low	Moderate	Moderate
Coolidge-Wellton-Antho. Deep, moderately coarse-textured soils on lower alluvial fans and valley plains; from schist, granite volcanic, and sedimentary sources	61+ m	18m	7.4 - 8.4	Moderately Rapid	Moderate	Moderate	Moderate
Lomitas-Rock Outcrop. Shallow stony soils and rock outcrop; from various sources	91 - 884m	30 – 51m	7.4 - 8.4	Moderate	Very Low	Slow	High

[1] Underlined soil series are generalized grouping of principal associated soils as they occur on the landscape; they include minor soils. The classification is indented only for general planning use.

[2] pH is the degree of acidity or alkalinity of a soil.

-Gunsight Association (HPGA), except they are more sandy than the gravelly soils of the HPGA. The most dominant soil type at the YPG is the HPGA; these soils cover most of the Cibola and Kofa Firing Ranges and consist of deep, gravelly, moderately fine textured soils high in lime concentrations, and very gravelly calcareous soils found on old alluvial fans (Entech Engineers, Inc., 1988). The mountain areas consist generally of soils noted as Lomitas-Rock-Outcrop Association, which are mostly of volcanic rocks, including andesite, rhyolite and related tuffs, and some basalt (Entech Engineers, Inc., 1988).

All of the soils within the YPG, with the exception of the Lomitas-Rock-Outcrop Association, are considered to have moderate infiltration rates and runoff potential. The Lomite-Rock-Outcrop Association soils have slow infiltration rates and high runoff potential (Table 2); however, in the YPG area, the potential is generally poor because of low precipitation.

Little information exists on the mineral resources of YPG. Existing information pertains to approximately one-fourth of YPG that is not covered by alluvium (U.S. Corps of Engineers, 1988). Relatively small deposits of gold, copper, silver, lead, manganese, and tungsten have been located and mined in the region. Around the YPG area, the following metals are noteworthy: antimony, beryllium, cadmium, copper, gold, lead, manganese, mercury, silver, titanium, tungsten, uranium, vanadium, and zinc; non-metals include only barite and fluorite. Regarding fuels, coal does not occur in southwest Arizona. No occurrence of either oil or natural gas has been located (U.S. Corps of Engineers, 1988).

2.5.7 Geology

As stated earlier, YPG is situated in the basin and range of physiographic province (Figure 16). The mountain ranges within and surrounding YPG are composed of igneous rocks, including extrusive and intrusive ones; sedimentary rocks; and metamorphic rocks (U.S. YPG, 1999). The Palomas and Tank mountains contain mostly extrusive igneous rocks with smaller amounts of metamorphic. Intrusive igneous rocks are also found in the southern part of the Palomas Mountains. The Muggins Mountains are made up of metamorphic and extrusive igneous rocks with some sedimentary rocks; while the Middle Mountains are composed of mostly extrusive igneous rocks with metamorphic and sedimentary rocks. The Trigo and Chocolate Mountains are largely extrusive igneous rocks with some metamorphic ones.

The basins of lowlands between mountain ranges are composed of alluvium, which is typically sand, silt, and clay layers that were deposited during the Quaternary Period (3 million years ago). The surface and subsurface geology at the YPG range from consolidated rocks of hard, dense, crystalline ores, such as gneiss, schist, and granite to volcanic rocks. The unconsolidated rocks consist of a younger and older alluvium, separated by a marine deposit, to flood-plain deposits along the Colorado River (Entech Engineers, Inc., 1988). Figure 19 illustrates a geologic stratigraphic column of YPG areas showing the inferred stratigraphic relations of these units. Figure 20 presents the generalized geology of the YPG, while Figure 21 highlights two generalized cross-sections that transverse YPG from southwest to northeast.

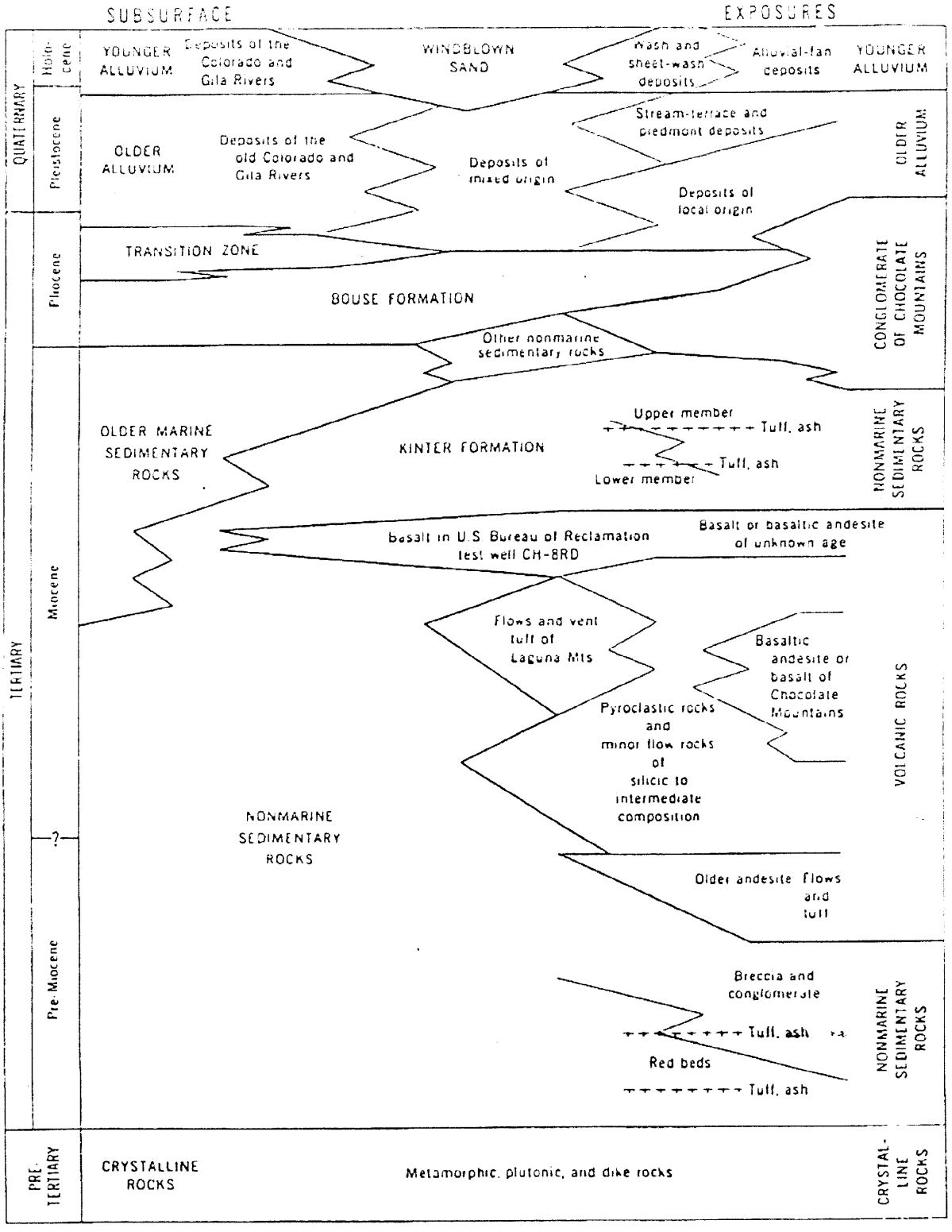

Figure 19 Stratigraphic Column of Yuma Area and YPG (Olmstead et al., 1973)

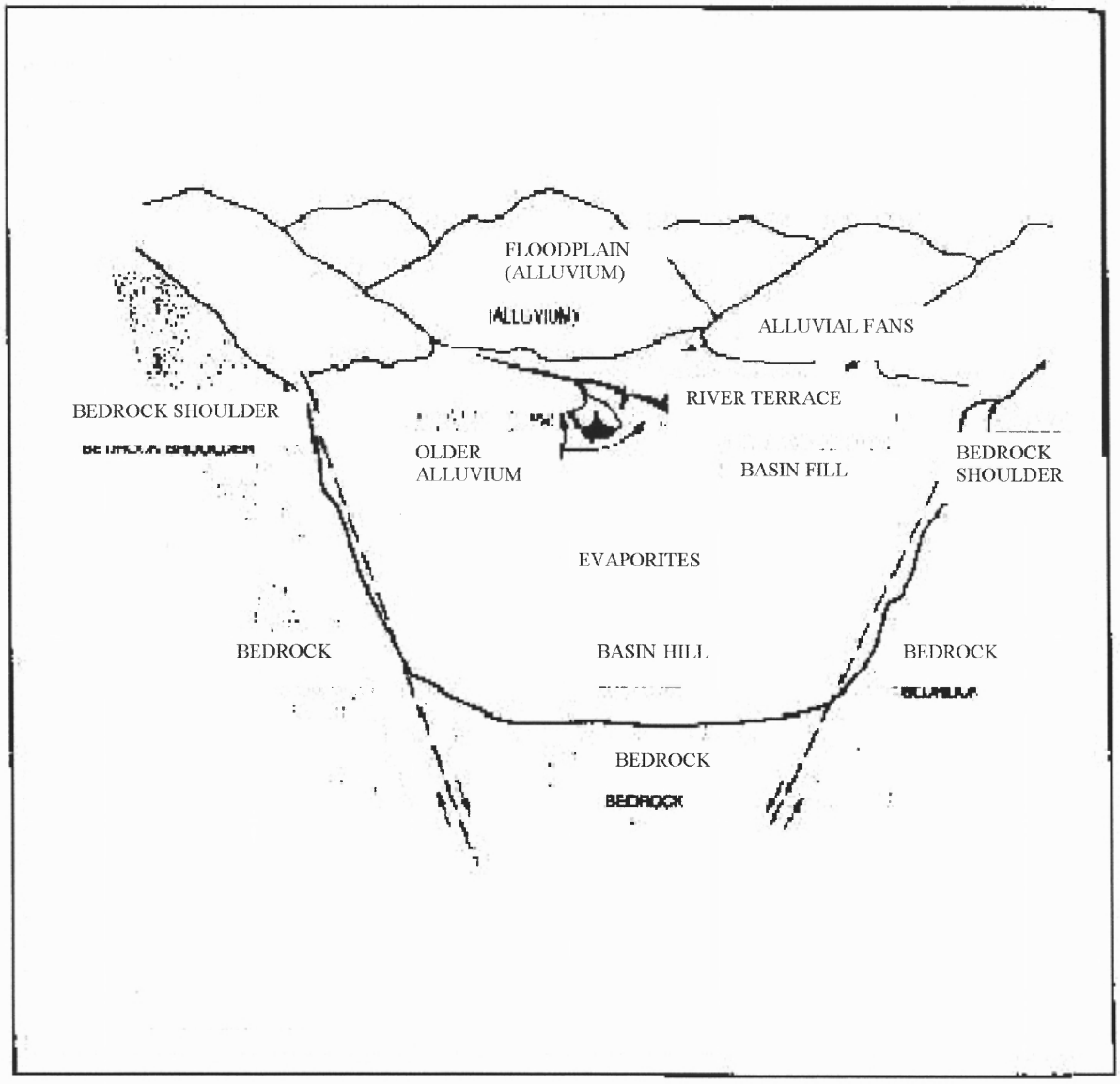

Figure 20 Cross Section of Yuma Proving Ground Generalized Geology (U.S. Army YPG, 1999)

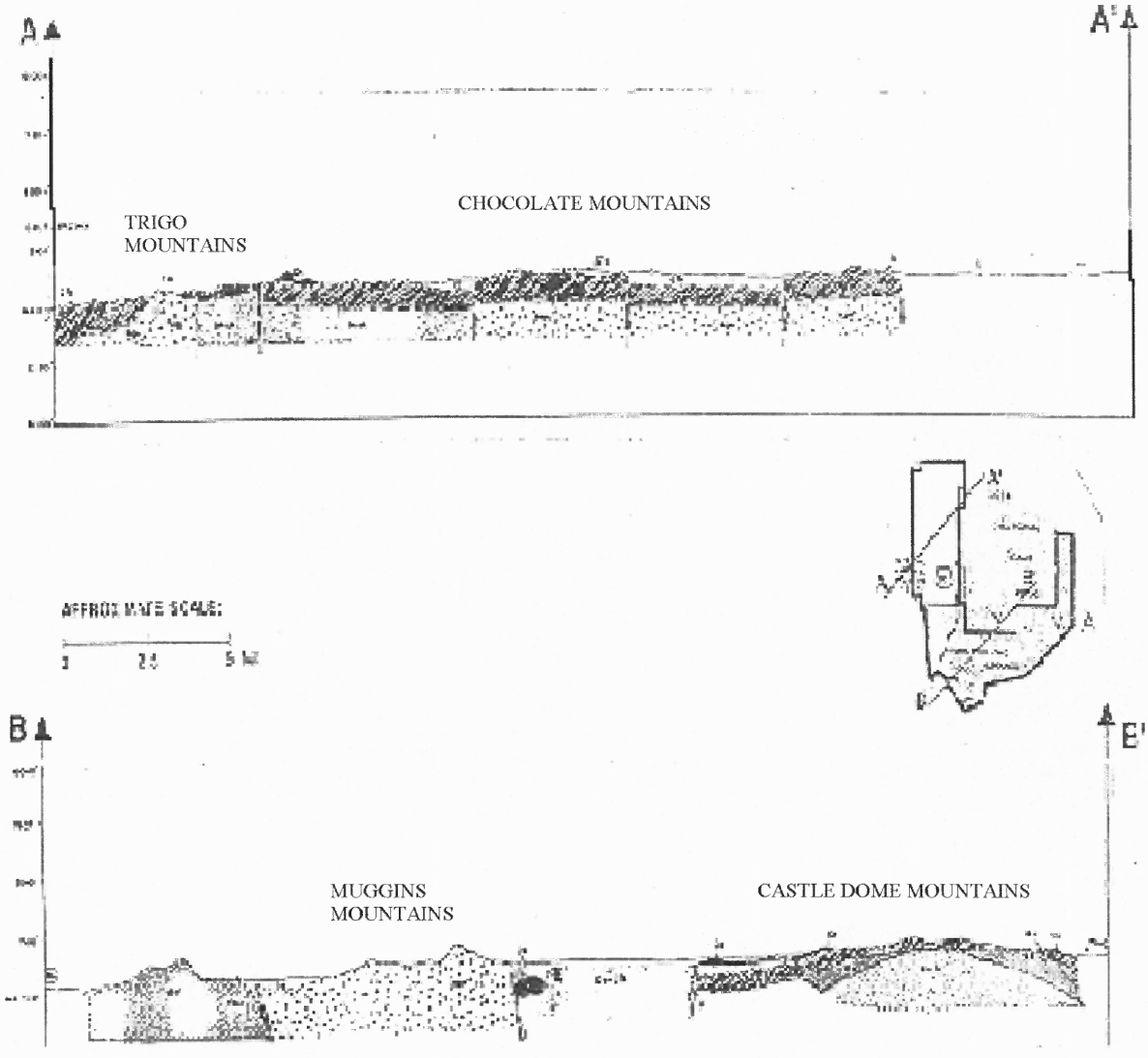

Figure 21 Generalized Geologic Cross-Section across YPG Area (Entech Engineers, Inc., 1988)

2.5.8 Groundwater

The Army uses well water for domestic and industrial operations. The main water yielding units are alluvial deposits (Click and Cooley, 1967), which are replenished by the Colorado and Gila Rivers. Local precipitation and runoff are minor sources of groundwater recharge. As a result, the recharge is affected by precipitation in the mountain upstream from YPG.

During the period 1961-66, the USGS inventoried 936 wells in the Yuma area (Olmsted, 1973). Most of the wells were in the Yuma valley and Mesa areas and along the Gila River. Several wells are in the YPG and scattered from the Castle Dome Heliport to the southwest toward the Gila and Colorado Rivers, and illustrated as characters "B-Y" in Figure 22. These wells have provided most the useful data for the ground water hydrology study in this area (Table 3). Among these wells, X and Y yield the most ground water at rates of 800 – 100 gallons per minute (gpm). The rest of the wells each yield between 50 – 200 gpm (Entech Engineers, Inc., 1988). Aquifer hydraulic parameters including transmissivity and hydraulic conductivity were derived from studying these wells (Table 4). The direction of ground water flow is southwest towards the Colorado and Gila Rivers; the ground water gradient of the major pumping centers is about 4-5 feet per mile, and less than 4 feet per mile near the Colorado and Gila Rivers. The depth to ground water in the aquifer beneath the YPG, as measured in YPG wells, ranges from 30-35 feet below land surface at wells X and Y, which are located adjacent to the Colorado River, to 635 feet below land surface at well M on the Castle Dome (Entech Engineers, Inc., 1988). Table 5 shows the depth to ground water and mean level elevations as measured in the YPG wells from 1952 – 87.

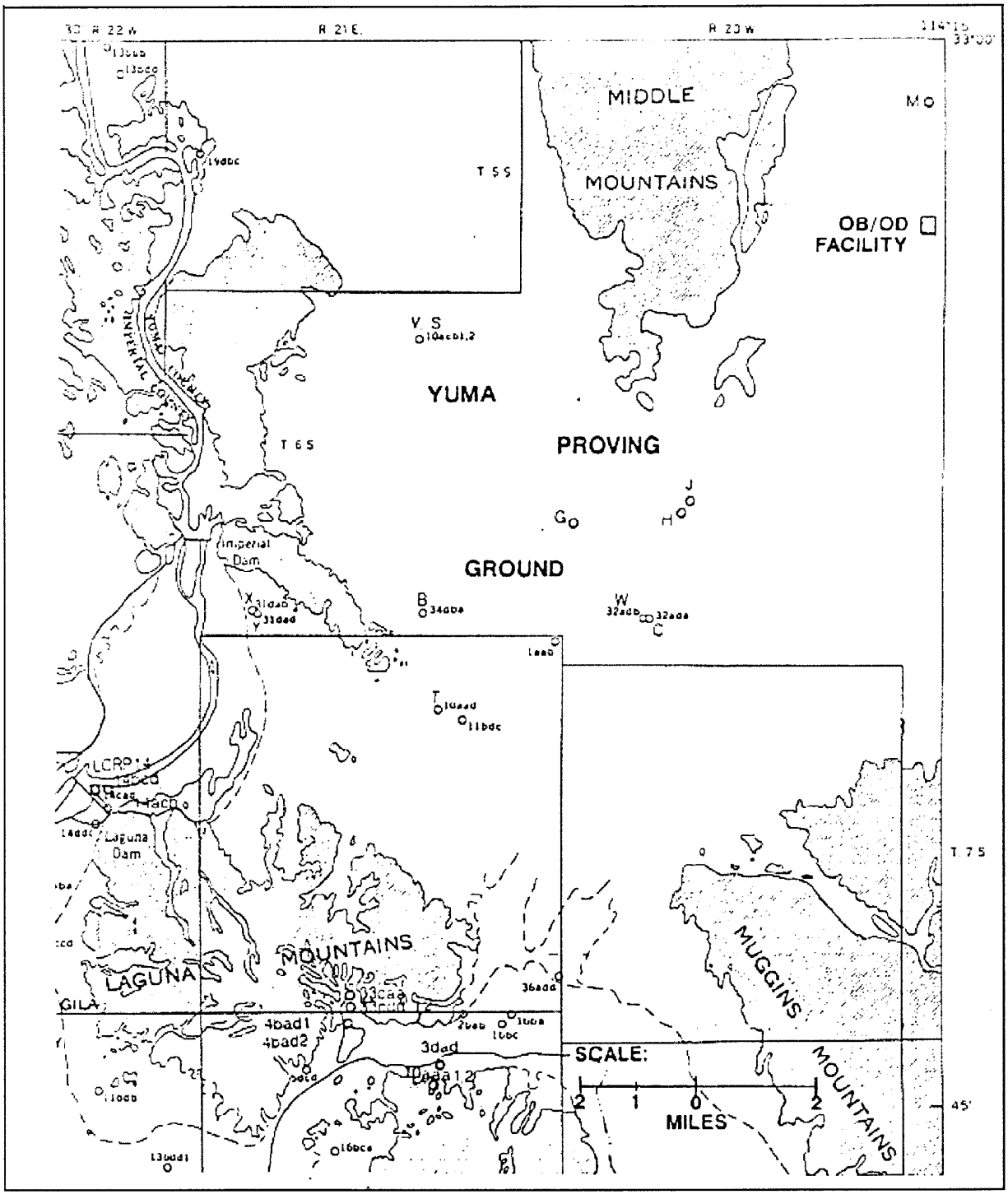

Figure 22 Wells Around YPG: Well B, C, G, H, J, M, S, T, U, V, W, X and Y (Entech Engineers, Inc., 1988)

Table 3 Wells Information of YPG (See Figure 22 for well location) (Entech Engineers, Inc., 1988)

WELL	DATE DRILLED	DEPTH (ft.)	DEPTH TO WATER (feet)	SURFACE ELEVATION (ft above msl)	OPERATION STATUS	DISCHARGE CAPACITY (gpm)
B	1958	271	203	363	in use	170
C	No data				abandoned	
G	1958	400	300	450	in use	100
H	1959	502	322	500	in use	170
J	1971	502	331	500	in use	200
M	1969	1000	750	833	in use	170
S	1960	300	211	382	in use	65
T	1952	282	163	332	abandoned	200
U	1952	397	165	327	in use	200
V	1968	340	210	382	in use	35
W	1967	503	265	411	in use	200
X	1952	308	30	184	in use	980
Y	1959	141	35	182	in use	980

Note: (1) Depths to water taken from the most recent recording

Table 4 Aquifer Parameters of YPG (Entech Engineers, Inc., 1988)

Well	Transmissivity gpd/ft		Penetrated Saturated Thickness	Hydraulic Conductivity gpd/sq.ft
	(1)	(2)	(3)	(4)
B	58,800	none	67	878
G	77,330	156,200	108	715
H	64,000	none	172	372
M	9,600	none	171	56
S	65,000	none	72	902
T	41,700	none	127	328
U	83,300	none	292	285
W	19,000	none	228	83
X	130,800	none	105(5)	1,245

Notes:
(1) Empirical values obtained from specific capacity data
(2) Value obtained from pump test data
(3) Value obtained from YPG well records (no date)
(4) Values obtained by dividing empirical transmissivity by the penetrated saturated thickness of permeable sediments.
(5) Using Well Y data.

Table 5 The Depth to Ground Water and Mean Level Elevations as Measured in the YPG Wells from 1952 – 87 (Entech Engineers, Inc., 1988)

DATE	WELL B	WELL G	WELL H	WELL J	WELL X	WELL M	WELL S	WELL T	WELL U	WELL V	WELL W	WELL X	WELL Y
04/52								164(168)	154(173)				
07/52												152 (32)	
10/52											166(245)		
10/56								164(168)	156(171)		166(245)		
12/58		158(292)											
04/59			170(330)										
05/60	164(199)												
09/60							172(210)						
13/60													149 (33)
04/61								164(168)	156(171)	172(210)	166(245)	152 (32)	
10/62													
13/69						199(634)							
02/70						197(636)							
12/71					306 (?)								
07/72	160(203)					293(540)							149 (33)
03/73													
13/82		150(300)											
04/84			174(326)					169(163)	166(161)		173(238)		
12/84	160(203)												
13/84											161(250)		
08/85				169(331)					160(167)	172(210)	146(265)	152 (32)	147 (35)
09/85			179(321)	167(333)					162(165)	172(210)	146(265)	152 (32)	147 (35)
10/85			179(321)	167(333)		83(750)			160(167)	175(207)	147(264)	154 (36)	147 (35)
11/85			179(321)	167(333)					162(165)	172(210)	146(265)	153 (31)	147 (35)
12/85			178(322)	165(335)					163(164)	175(207)	146(265)	152 (32)	147 (35)
01/86				169(331)		83(750)			162(165)	172(210)		152 (32)	147 (35)
02/86				167(333)		83(750)			160(167)	172(210)		152 (32)	147 (35)

According to these measurements, the depth to ground water in the aquifer beneath most areas of YPG is greater than 150 feet. This depth is an asset in preventing contamination. As a result, the water quality of the ground water does not appear to be influenced by the activity in the proving ground, based on chemical constituents analyzed to date (Entech Engineers, Inc., 1988). The depth to water adjacent to the Colorado River is less than 40 feet below land surface, but the high recharge capability of the Colorado River may dilute potential degradation of the water quality. In addition, the low precipitation and high evaporation prevents significant infiltration.

2.5.9 Ecology

Unlike the diverse ecosystems at Aberdeen Proving Ground, YPG located in the lower Sonoran Desert, is characterized by a terrestrial ecosystem, which consists of desert plants, wildlife, and habitats (Figure 23). The extreme aridity characterizing this regions is reflected in open plains covered sparsely with drought-tolerant shrubs, grasses, and cacti. Most common is the creosote bush. Sandy soil formations support large galleta grass communities along with foothill paloverde trees, honey mesquite trees, or bursage. Hillsides support brittlebush in various combinations with other plants such as cacti, especially the saguaro cactus. Foothill and mountains provide habitat for mixed shrubs. Desert washes support many trees, including the paloverde, ironwood, smoke tree, mesquite, and catclaw acacia. Open terrain area used for testing is covered with the creosote-bursage vegetation (Terner, 1994; Shreve, 1964).

Figure 23 Desert Environments Around Yuma Proving Ground

There are also many typical desert animals living around the proving ground. The most common types of wildlife include game mammals and birds, predatory and fur-bearing mammals, and migratory and resident birds. Large game animals are desert bighorn sheep and mule deer. Predatory and fur-bearing mammals includes the coyote, kit fox, black-tailed jackrabbit and gray fox. Badger, striped skunk, mountain lion, and bobcat can also be found randomly in this area. Moreover, at least 16 species of bats are known to occur on post (Castner et al., 1995). Among these plants and animals identified, selection of the characteristic receptors for the ERA will be discussed in the following section.

2.6 Ecosystem Animal and Plant Receptors

Considering the large area of YPG and the great diversity of the APG ecosystem, a significant amount of wildlife species live within the two sites. The following describes the process to select the appropriate species to be assessed.

2.6.1 Criteria

The principal criteria used to select the appropriate animals and plant receptors for risk assessments include the following (U. S. EPA, 1998):

- Ecological relevance, which means ensuring each major group of species is represented.
- Susceptibility to known or potential stressors, those receptors most likely to be exposed to contaminants.

- Relevance to management goals, those receptors of high concern for cultural and natural resource management reasons.

Based on these three general criteria, an initial list of species was assembled that included terrestrial and aquatic plant and animal receptors known to occur in the habitats of Yuma and Aberdeen Proving Grounds. This initial list was developed by selecting species from databases and records maintained by the following federal and state resource management agencies associated with the two proving grounds:

- U.S. Fish and Wildlife Service, Chesapeake Bay Field Office (U.S. Fish and Wildlife Service, 1999)
- U.S. Fish and Wildlife Service, Division of Endangered Species (U.S. Fish and Wildlife Service, 1991)
- U.S. Fish and Wildlife Service, Imperial National Wildlife Refuge (U.S. Department of the Interior, 1994)
- U.S. Fish and Wildlife Service, Kofa National Wildlife Refuge (U.S. Department of the Interior, 1996)
- Arizona Game and Fish Department (Arizona Game and Fish Department, 1988)
- U.S. Geological Survey, Activities in the Chesapeake Bay Region (U.S. Geological Survey, 1999)
- U. S. Army Yuma Proving Ground, Environmental Division (U.S. Army YPG, 1999)
- U.S. Army Garrison Aberdeen Proving Ground, Environmental Conservation & Restoration Division (U.S. Army Garrison APG, 1998)

Species distribution and habitat preferences were also obtained from these agencies. However, the majority of information was obtained from the U.S. Fish and Wildlife Service and the two proving grounds environmental divisions.

One hundred and fourteen species at APG and 30 species at YPG were identified for the study areas (Tables 6 and 7). As seen in Table 6, wildlife around APG includes 33 bird species, 11 mammal species, 9 aquatic animals, 6 reptile species, 7 amphibian species, 17 grassy plants, 18 tree species, 4 shrub/scrub species, 6 herbaceous species, and 3 woody species. On the other hand, in Table 7, the wildlife living in desert environment at YPG includes 9 mammal species, 5 reptile and amphibian species, 7 bird species, and 9 desert plants.

The rationale for a limited number of species in an ecological risk assessment is that among the major taxonomic groups (amphibian, bird, fish, insect, mammal, plant, reptile, etc.) presented in the tables, many have similar life styles (either fully aquatic, semi-aquatic, or terrestrial) and belong in the same trophic levels (carnivore, herbivore, omnivore, etc.). Where such similarities exist, these species likely contact contaminated media in much the same way. Thus, their potential exposure to contaminant is expected to be similar (Pacific Northwest National Laboratory [PNNL], 1998). Also, much of the data required to estimate contaminant exposure and the resulting adverse effects for many of the species on the initial lists are lacking, which would greatly increase uncertainty in the risk assessment. Because of the redundancy in exposure and increased uncertainty for which data are lacking, the study area species on the initial list were reduced further through use of additional criteria recommended by the U.S. EPA and PNNL Columbia River Comprehensive Impact Assessment (CRCIA) Management Team Representatives

Table 6 Aberdeen Proving Ground Wildlife (I)

ANIMALS (66)	
Birds (33)	General species: mallard, ring-billed gull, morning dove, red-bellied woodpecker, downy woodpecker, barn swallow, carolina chickadee, carolina wren, bluebird, American robin, European starling, Northern cardinal, song sparrow, red-winged blackbird, common grackle, wild turkey Waterfowl: black duck, wood ducks, blue-winged teal, hooded mergansers, and Canada geese (most abundant),American black duck, canvasback , and redhead Birds of pray: American Kestrel, eastern screech owl, great horned owl, barred owl, turkey vulture, and red-tailed hawk Endangered species: peregrine falcon, bald eagle
Mammals (11)	General species: white-tailed deer, cottontail rabbit, gray squirrel, beaver, striped skunk, white-footed mouse, Norway rat, opossum, raccoon, woodchuck Endangered species: delmarva fox squirrel, Indiana bat
Aquatic Animals (9)	Mayfly, mussels, clams, carp, rainbow, American eel, striped bass
Reptiles (6)	Spotted turtle, eastern mud turtle, common snapping turtle, eastern box turtle, northern water snake, eastern garter snake.
Amphibians (7)	Bullfrog, green frog, northern cricket frog, northern spring peeper, southern leopard frog, fowlers toad and red-backed salamander.
PLANTS (48)	
Grassy Plants (17)	Cattails, soft rush, pickerel weed, sedges, bulrush, nuphar, switch grass, common boneset, spikerush, wool-grass, asters, swamp milk reed, and stiff marsh bedstraw, redhead grass, eelgrass, widgeon grass, musk grass
Tree Species (18)	Red maple, sweet gum, willow, American elm, ashes, pin oak, and swamp chestnut oak, white oak, southern red oak, black oak, northern red oak, beech, sweet gum, yellow poplar, sycamore, black cherry, and black locust Endangered Species: slender blue flag
Shrub/ Scrub Species (4)	Groundsel bush, wax myrtle, dewberry, and Japanese honeysuckle
Herbaceous Species (6)	Bluegrass, timothy, yarrow, goldenrod, plantain, and brome grass
Woody Species (3)	Blackberry, honeysuckle, and grape

Table 7 Yuma Proving Ground Wildlife (I)

ANIMALS (30)	
Mammals (9)	Kit fox, wild horses, wild burros, black-tailed jackrabbit, cactus mouse, mule deer, white-tailed deer, bighorn sheep, lesser long-nosed bat, coyote
Reptiles and Amphibians (4)	Western coral snake, desert tortoises, common king snake, desert spiny lizard,
Birds (7)	Rail (Yuma clapper), Mexican spotted owl, loggerhead shrike, cactus wren, gambel's quail, peregrine falcon, bald eagle
PLANTS (9)	
Cactus (2)	Nichol's Turk's head cactus, saguaro cactus
Shrub/ Scrub Species (4)	Creosote bush, desert lily, crucifixion thorn, bursage
Tree Species (3)	Paloverde trees, ironwood, catclaw acacia

(MTR) (PNNL, 1998). These criteria were developed for screening the study area species and include the following:

1. Commercial or recreational importance.
2. Protection status under the Endangered Species Act or similar state legislation.
3. Critical component of ecosystem: key predator or prey.
4. High potential exposure to contaminants.
5. Availability of toxicological information for the species.
6. Representatives of a foraging guild.

The initial list of receptors was evaluated with these criteria based on their cultural and ecological importance and the possibility that they virtually occur in study

Table 8 Aberdeen Proving Ground Wildlife (II)

	Criteria 1	[4]Criteria 2	Criteria 3	Criteria 4	Criteria 5	Criteria 6	Total Positive Marks	Final Species
[1]**Birds**								
[2]Mallard	+	-	-	+	+	+	4	*
Barn swallow	-	-	+	-	+	-	2	
Red-winged blackbird	-	-	-	+	-	+	2	
Canada geese	+	-	-	+	+	-	3	N
[2]Black duck	+	-	-	+	+	-	3	N
American Kestrel	-	+	+	-	+	+	4	*
Barred owl	-	-	+	+	+	+	4	*
American robin	-	-	-	+	-	+	2	
Bald eagle	-	+	+	+	+	-	4	*
Peregrine falcon	-	+	+	-	-	-	2	
Morning dove	-	-	-	+	-	-	1	
European starling	-	-	-	+	-	+	2	
[3]Canvasback	+	-	+	+	-	+	4	N
Song sparrow	-	-	-	+	-	+	2	
Wild turkey	+	-	-	-	-	+	2	
Red-tailed hawk	-	+	-	-	-	+	2	
Ring-billed gull	-	+	-	-	-	-	1	
Mammals								
Indiana Bat	-	+	+	+	-	+	4	*
Delmarva fox squirrel	-	+	-	+	-	-	2	
White-tailed deer	-	+	+	-	+	+	4	*
Cottontail Rabbit	+	-	-	+	+	+	4	*

Table 8 (Continued)

	Criteria 1	[4]Criteria 2	Criteria 3	Criteria 4	Criteria 5	Criteria 6	Total Positive Marks	Final Species
Mammals								
Norway rat	+	-	+	+	+	+	5	N
Striped skunk	-	-	+	-	-	-	1	
White-footed mouse	+	-	+	+	+	+	5	*
Beaver	-	-	+	+	+	+	4	*
Raccoon	+	-	-	+	-	-	2	
Woodchuck	+	-	+	-	-	-	2	
Aquatic animals								
Clams	+	-	-	+	-	-	2	
Mountain whitefish	+	-	-	+	+	-	3	*
Pacific Lamprey, juvenile	+	-	-	+	+	-	3	*
Carp	+	-	+	+	-	+	4	N
American eel	-	-	-	+	-	+	2	
White sturgeon	+	-	+	+	+	+	4	*
Rainbow	+	-	+	+	+	-	4	*
Reptiles								
Common snapping turtle	-	-	-	+	+	-	2	
Black rat snake	-	-	+	+	+	+	4	N
Eastern garter snake	-	+	+	+	+	+	5	*
Lizards	+	-	-	+	+	-	3	*
Amphibians								
Bullfrog	+	-	-	+	+	+	4	N
Fowlers toad	-	-	+	+	-	-	2	
Green frog	-	+	+	-	+	-	3	N

Table 8 (Continued)

	Criteria 1	[4]Criteria 2	Criteria 3	Criteria 4	Criteria 5	Criteria 6	Total Positive Marks	Final Species
Amphibians								
Red-backed salamander	-	+	-	-	-	+	2	
Woodhouse's toad	-	-	-	+	+	+	3	*
[1]**Aquatic plants**								
Water millfoil	+	-	-	+	+	+	4	*
Eelgrass	-	-	-	+	-	+	2	
Phytoplankton	+	-	+	+	+	+	5	*
Periphyton	-	-	+	+	+	+	4	*
Stiff marsh bedstraw	-	-	-	+	-	+	2	
Terrestrial plants								
Red maple	+	-	+	-	-	-	2	
Fern	-	-	+	+	+	+	4	*
Rushes	-	-	+	+	+	+	4	*
Slender Blue Flag	-	+	-	+	-	+	3	*
Cattail	-	-	+	+	-	+	3	N
Sweet gum	-	-	+	+	-	+	3	N

Note:
+ positive respond to the criteria
- negative respond to the criteria
* Species in the Final list
N Species with a life style and exposure scenario similar to that of another List II species:

References:
[1] Munro, et al. 1982 ; Robbins et al., 1968
[2] Krementz et al, 1991, 1992
[3] Haramis et al,.1994 ; Perry et al., 1988
[4] Arizona Game and Fish Department, 1988; Martin et al., 2000; U.S. Fish and Wildlife Service, 1991

Table 9 Yuma Proving Ground Wildlife (II)

	Criteria 1	[6]Criteria 2	Criteria 3	Criteria 4	Criteria 5	Criteria 6	Total Positive Marks	Final Species
[1]**Mammals**								
[2]Lesser long-nosed bat	_	+	+	+	-	+	4	*
Cactus mouse	-	-	+	+	+	+	4	*
Kit fox	-	-	+	-	+	+	3	*
Black-tailed jackrabbit	+	-	+	+	+	+	5	*
Wild horses	-	-	+	+	+	+	4	N
Wild burros	-	-	+	+	-	-	2	
Mule deer	-	+	+	-	+	+	4	*
White-tailed deer	-	+	+	-	+	+	4	N
[3]Bighorn sheep	-	+	+	+	-	+	4	N
Birds								
Rail	-	+	-	-	-	+	2	
Peregrine falcon	-	+	-	-	-	-	1	
Bald eagle	-	+	-	-	+	-	2	
Mexican spotted owl	-	-	+	+	+	+	4	*
Loggerhead shrike	+	-	-	+	+	+	4	*
Gamble's quail	+	-	-	+	+	+	4	*
Cactus wren	-	-	-	+	-	+	2	
[4]**Reptile & amphibian**								
Desert tortoise	-	+	+	+	-	-	3	*
Sonora whipsnake	-	-	+	+	+	+	4	*
Western coral snake,	-	-	+	+	-	+	3	N
Desert spiny lizard	-	-	+	+	+	-	3	*

Table 9 (Continued)

	Criteria 1	[6]Criteria 2	Criteria 3	Criteria 4	Criteria 5	Criteria 6	Total Positive Marks	Final Species
[5]Plants								
Nichol's Turk's head cactus	+	-	+	-	-	+	3	N
Saguaro Cactus	-	-	+	+	+	+	4	*
Creosote bush	-	-	+	+	+	+	4	*
Desert Lily	-	-	+	+	-	-	2	
Crucifixion Thorn	-	-	+	+	-	-	2	
Foothill paloverde trees	-	-	+	+	+	+	4	*

Note:
+ positive respond to the criteria
- negative respond to the criteria
* Species in the Final list
N Species with a life style and exposure scenario similar to that of another List II species

References:
[1] Hoffmeister, 1986
[2] Caster et al., 1995
[3] Monson et al., 1990
[4] Stebbins, 1985
[5] Benson et al, 1981 ; Jaeger, 1969 ; Shreve et al, 1964 ; Terner et al. 1994
[6] Arizona Game and Fish Department, 1988; Martin et al., 2000; U.S. Fish and Wildlife Service, 1991

area. Results from the analysis are presented in Tables 8 and 9, where a positive (+) or negative (-) response is illustrated. With three or more positive responses, a species was short-listed as a final target receptor with a (*) in the right-hand column. For an indicator (N) in the right-hand column, the species was not selected for the reasons that their life styles are close to another species selected. Among the wildlife of APG, Canadian geese, black duck and canvasback are similar to the mallard; Norway rat is similar to white-footed mouse; carp is similar to white sturgeon; back rat snake is similar to eastern garter snake; green frog and bullfrog are similar to woodlouse's toad; and, cattail and sweet

gum are similar to the other selected terrestrial plants. Among the wild life of YPG, white-tailed deer, wild horse, and bighorn sheep are similar to mule deer; western coral snake is similar to Sonora whipsnake; and, the Nichol's Turk's head cactus is similar to saguaro cactus. For undesignated species, the positive responses are less than three and they are not included in the model.

2.6.2 Final Receptors

The 57 species of APG were reduced to 23. For YPG, the 23 species were reduced to 14 excluding 1) those with low score, and 2) those with a life style similar to that of another species selected. Among these receptors, Indiana bat at APG, and the lesser long-nosed bat, desert tortoise, and Mexican spotted owl at YPG are species designated as threatened, endangered, and sensitive species by U.S. Army (Martin et al., 2000). The final selected receptors for the two sites are shown in Table 10.

2.7 Summary

In this chapter, guidance for identifying and selecting parameters for an ERA has been presented and the site specific characteristics and associated receptors for the assessment have been reviewed. Because of the diverse ecosystem around Aberdeen Proving Ground, both terrestrial and aquatic species will be considered in the future ecological risk assessment. YPG is characterized by a typical desert ecosystem. Accordingly, the receptors for the assessment are focused on the terrestrial species. These site data provide the means for assessing transport and potential exposure pathways for the concerned sites.

Table 10 Final Receptors of Aberdeen Proving Ground & Yuma Proving Ground

	APG		YPG	
	Receptors	Amount	Receptors	Amount
Birds	Mallard, American kestrel, barred owl, bald eagle	4	Mexican spotted owl, loggerhead shrike, gamble's quail	3
Mammals	White-tailed deer, beaver, white-footed mouse, cottontail rabbit, Indiana bat	5	Kit fox, cactus mouse, black-tailed jackrabbit, mule deer, lesser long-nosed bat	5
Reptiles & Amphibians	Eastern garter snake, lizards, woodhouse's toad	4	Desert tortoises, sonoran whipsnake, desert spiny lizard	3
Aquatic Animals	Mountain whitefish, pacific lamprey, white sturgeon, rainbow	4		
Aquatic Plants	Water millfoil, phytoplankton, periphyton	3		
Terrestrial Plants	Fern, rushes, slender blue flag	3	Creosote bush, foothill paloverde trees, saguaro cactus	3

CHAPTER 3

ERA MODEL DEVELPOMENT

3.1 Introduction

Assessing the potential for adverse effects in ecological receptors due to contact with environmental contaminants at concerned areas requires the estimation of exposure. Such exposure characterization is a critical step in the ecological risk assessment (ERA) process; it can be used to (Hope, 1995):

- Provide an initial estimate of ecological receptor exposure to site related contaminants present in surface water, groundwater, sediment, soil, and air media. Results may be used to guide future sampling efforts that would contribute to a baseline assessment.
- Estimate dose to, and tissue concentrations in, higher trophic level or protected species, which cannot or should not be sacrificed to obtain tissue samples for chemical analysis.
- Support development of data quality objectives by indicating whether proposed detection limits are low enough to encompass media and tissue concentrations of ecotoxicological interest.

In an effort to create a more generalized model that can be easily adapted to varying ecosystems, all potential exposure pathways are included and options to modify site-specific conditions will be provided. This chapter presents the quantitative exposure estimations considered in the ERA model that, given a specified set of possible exposure pathways and routes, can be combined to produce site- and species- specific estimation of contaminant uptake from abiotic as well as biotic media. First, a literature review is

presented on exposure assessments based on laboratory and field studies. Results from these studies help elicit mechanisms responsible for contaminant uptake. Following that, quantitative measurements are identified for estimating potential exposure and associated algorithms and parameters are defined. Risk is characterized for the exposure estimate results. Subsequently, these algorithms were written in Visual Basic (VB) and integrated into the VB interface that is linked to an interactive DBMS. The ERA model is verified with a range of contaminants concentrations.

3.2 Uptake of Contaminants

Contaminant uptake mechanisms involve complex processes and are influenced by receptors, chemical speciation, and environmental conditions. To better understand exposure pathways, the fundamental uptake mechanisms for plants and animals based on laboratory and field studies are reviewed.

3.2.1 Contaminants Uptake by Plants

Uptake of contaminants by plants is a very complex process affected by contaminant physiochemical properties, environmental conditions, and plant characteristics. Elements occur in the soil in a variety of forms that are more or less available for uptake by plants (Efroymson et al., 1997). Many contaminants of concern at waste sites are metals or metalloids (Efroymson et al., 1997; Ross, 1994). Bioavailability is a function of chemical speciation, which affects the species mobility in the soil environment. Soil characteristics (e.g., pH, mineralogy, organic matter, and moisture content) affect metal speciation or availability to plants, which may involve temporary immobilization through interactions with mineral surfaces (e.g., adsorption-desorption processes), precipitation, and solid

solution formation (Efroymson et al., 1997). Particulate soil organic matter may serve to temporarily remove dissolved metals from the bulk aqueous phase, however, soluble organic matter may enhance mobility resulting in increased exposure to receptors like plants (Efroymson et al., 1997). Although metal contaminants may bind to exterior exchange sites on the root and not then be taken up, extensive studies have revealed that select plants uptake and translocate metals as well (Farago, 1994; Ross, 1994; Greger, 1999; Kelly et al., 1999; Sun et al., 1999; Zhang et al., 1999). Metals may enter the root passively in complexes or actively by way of metabolically controlled membrane transport processes where the contaminant mimics a nutrient (Efroymson et al., 1997). At different soil solute concentrations, both processes may play a part in metal uptake. Absorption mechanisms including the quantity absorbed are a function of the plant species (and cultivars), growth stage, physiological state, and the presence of other elements. Terrestrial plants uptake contaminants through the following routes:

1) Root uptake - transfer from the root to the above ground portions of the plant

2) Deposition of particle-bound contaminants on the leaves and fruits of plants

3) Vapor transfer - the vapor phase uptake of contaminants through their foliage.

Contaminants can be bound to particles and deposited on plant surfaces. Deposition includes sedimentation under the influence of gravity, impact under the influence of eddy currents, and deposition under the influence of precipitation (Treshow, 1984). Besides being bound to particles, contaminant absorption on foliage may also occur through vapor transfer via diffusion and advection. Subsequently, contaminant uptake is through the stomatal pores. These pores are present in the epidermal surface of leaves through which plants naturally exchange carbon dioxide, oxygen, and water vapor with the

atmosphere. The waxy cuticle of leaf surfaces restricts diffusion in that all gas exchange is via the stomatal opening. Even though these openings make up only approximately 1% of the leaf's surface area, their orientation and mechanics prove to be adequate for permeability.

Nevertheless, root uptake is the most important route by which most contaminants, especially metals, transfer to the aboveground portion of the plants (Farago, 1994). Many researchers (Bowling, 1976; Farago, 1986, 1994; Streit and Stumm, 1993) have discussed theories of mineral uptake by plant roots and identified four links in the uptake chain: movements of ions or complexes in the soil to the root surfaces; uptake into the roots; transfer across the root to the vascular system; and translocation to the above ground parts. The epidermis of the root has extensions in the form of root hairs, with a pectic coating, which allows them to adhere to soil particles. The hairs also greatly enhance the area of contact with the soil. Figure 24 shows a transverse section of a typical root. A large part of the root consists of relatively large and loosely arranged parenchyma cells, with air spaces, collectively known as cortex. The central portion of the root, the stele, contains the vascular system, which is responsible for the transport of food, water, and minerals throughout the plant. These tissues contain the xylem, which conducts water and nutrients up to the aerial parts, and the phloem, which functions as a conductor of organic material. The stellar portion of the root is surrounded by a layer of cells, the endodermis, which separates the stele from the cortex. The chief feature of the endodermis is the Casparian strip or band, which surrounds the

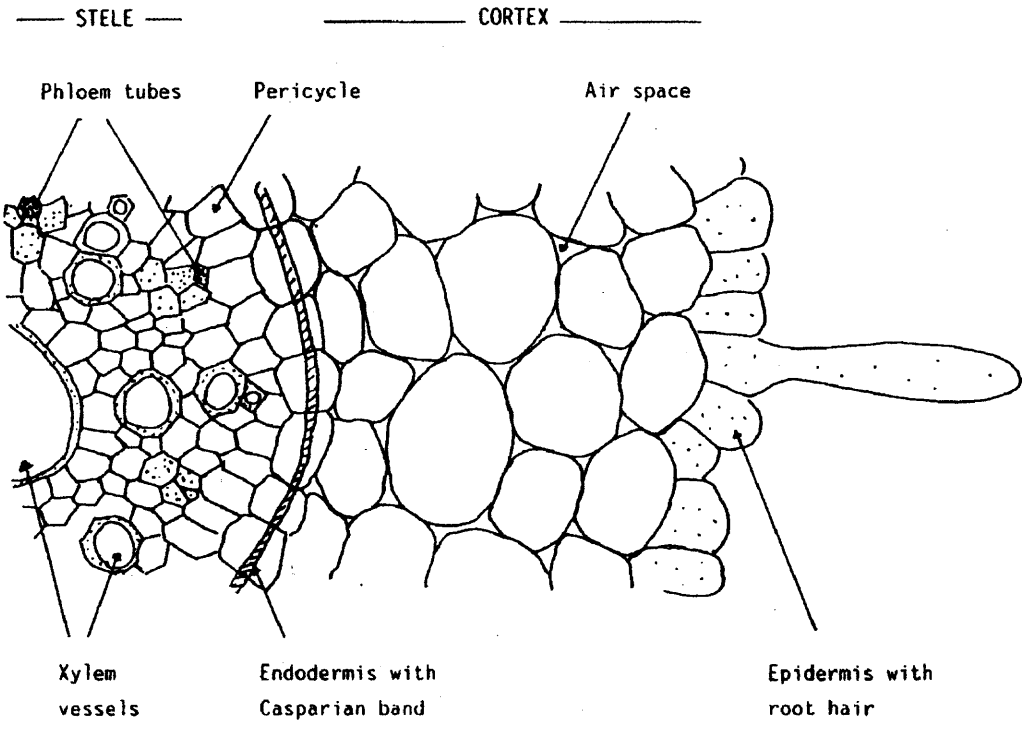

Figure 24 Transverse Section of a Typical Root (Farago, 1986)

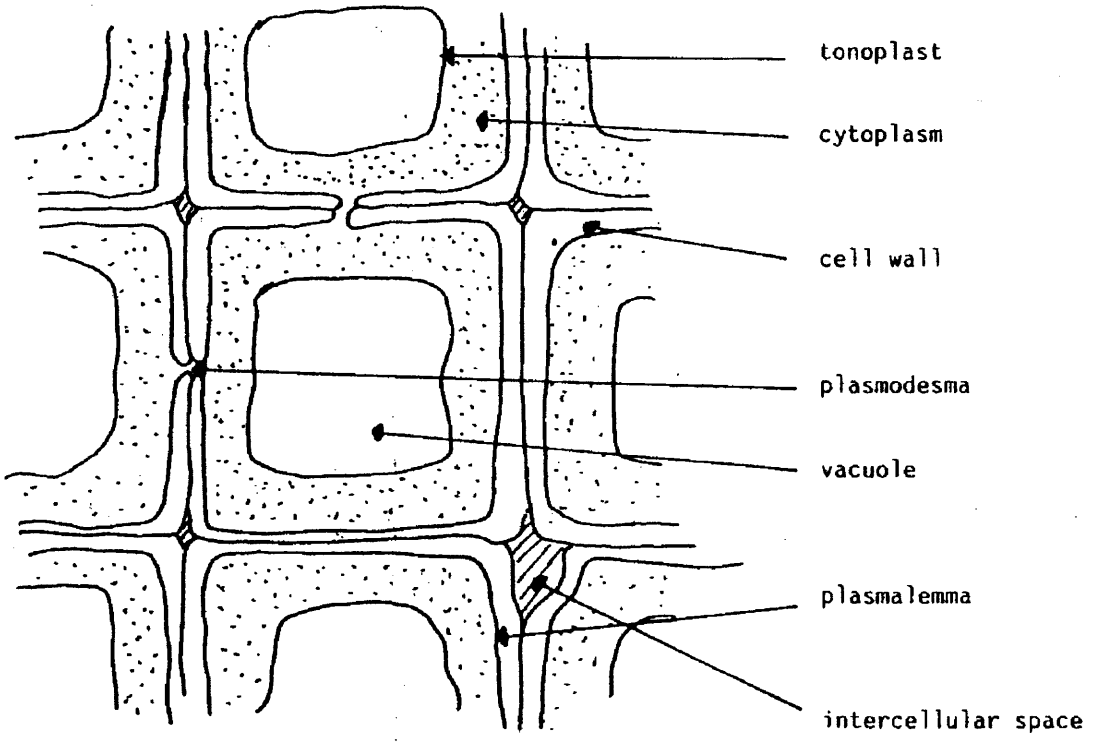

Figure 25 Typical Plant Cells (Farago, 1986)

walls of each cell. In order to reach the xylem, water and dissolved salts must pass through the living portions of the cells by diffusing through a membrane, the plasmalemma (Figure 25) (Farago, 1994).

The absorption of a species through the roots can be active (metabolic) and passive (non-metabolic). A number of metal ions diffuse passively in and out of the root to the Casparian band although uptake in some cases, such as K^+ and Na^+, by epidermal and cortex cells seems to be by active transport (Farago, 1994). Ions cross the root by two general pathways:

1. Cell wall pathway: ions cross the cortex by means of the cell walls.

2. Symplasm pathway: ions cross the cortex by cytoplasmic drift through the continuum of cytoplasm that extends from the cell through the plasmodesmata, and is known as the symplasm.

It is generally accepted that the xylem is the main path for transport of water and ions from the roots to the leaves. Most of the essential major elements are transported in the xylem as inorganic ions. Nitrogen may be transported along the xylem if it is present in the external solution as nitrate or ammonium (Farago, 1994). In the xylem, heavy metals are usually mobilized if chelates are formed, for example, with citrate (Streit and Stumm, 1993). However, further research is needed to verify contaminant fixation, translocation, and mobilization. Central to the goal is understanding chemical speciation, which is critical for modeling contaminant transport within a plant as well as an ecosystem. Since root uptake and translocation involves multiple processes including adsorption, precipitation, and complexation (Farago, 1994; Ross, 1994; Kelly et al., 1999), studies require noninvasive methods to evaluate contaminant speciation. For

example, Kelly et al. (1999) studied the mechanism of Eu(III) uptake by Water Hyacinth. They observed that as much as 8.7×10^{-4} mol Eu(III)/g dry root material was taken up from an initial solution of 3.3×10^{-4} M of Eu (III). Using scanning electron microscopy (SEM), they found that Eu (III) adsorbed on the root surfaces where the highest concentrations appeared to be on the root hairs. In this same study, X-ray absorption spectroscopy (XAS) was also used to look at Eu (III) speciation on the Water Hyacinth. Results suggested a Eu-oxygen environment, which likely involves binding of Eu (III) to the root via carboxylate groups and hydration of Eu (III) at the root surface (Kelly et al., 1999).

Research was also conducted to understand how contaminants affect plants after uptake. Metal accumulation by aquacultured seedlings of Indian mustard was studied using XAS (Salt et al., 1998). The research showed that compared with shoots, roots of Indian mustard (*B. juncea*) seedlings had a greater capacity to accumulate Cd. While shoots have limited capacity to adsorb Cd onto their cell walls, the function of the shoot in Cd uptake was not elicited. Lytle et al. (1998) also used XAS to study the reduction of Cr(VI) to Cr(III) by *Eichhornia crassipes* (water hyacinth). The study revealed that Cr(VI) supplied in the nutrient solution was rapidly reduced during uptake by the fine lateral roots. Subsequently, Cr(III) was translocated at a slower rate through the main roots than the leaves, however, further studies are needed to probe the associated mechanisms.

In addition, contaminant uptake by roots has been investigated as a function of their physical-chemical properties (benzene, toluene, ethylbenzene, m-xylene, nitrobenzene, 1,2,4-trichlorobenzene, aniline, phenol, pentachlorophenol, atrazine,

hexahydro-1,3,5-trinitro-1,3,5-triazine, and trichloroethylene) (Burken et al., 1998). Using hybrid poplar trees, Burken et al. found that root uptake was related to the logarithm of the compound's octanol-water partition coefficient (log K_{ow}). The interaction between the species and the root surface is a critical mechanism in translocation, for the chemical must pass the sumplast of the endodermis in order to translocate to the above ground parts of the plant. Compounds exhibiting lower hydrophobicity (log $K_{ow} < 1.8$) are not expected to pass through the lipid membranes associated with the epidermal layers of the roots. However, the more hydrophobic compounds with a log $K_{ow} > 1.8$, can enter the roots tissues, but do not enter the xylem for translocation from the roots to the shoots and the leaves. These compounds become bound to both the mucigel associated with the root surface and the lipid membranes of the root's epidermis. Hydrophobic compounds such as 1,2,4-trichlorobenzene (TCB) and pentachlorophenol (PCP), tend to absorb into the root tissues and were occluded from entering the translocation stream (Burken et al., 1998). On the other hand, compounds like aniline, hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and phenol, which are less hydrophobic, apparently did not pass through the organic membranes, and remained adsorbed on the external surfaces of the root.

Besides terrestrial, aquatic plants also provide a route for contaminants to enter the food chain due to their limited mobility, abundance in many aquatic systems, and high potential to sorb organic substances (Gobas et al., 1991). However, in contrast to terrestrial, most aquatic plants are non-rooted, free-floating macrophytes; therefore, contaminant uptake is represented by partitioning (Hope, 1995). As a result, exposure is often evaluated based on equilibrium (Davis et al., 1994). To estimate the aquatic plant

exposure, contaminant partitioning between surface waters and aquatic macrophytes is defined with contaminant-specific bioconcentration factors (BCF) (Davis et al., 1994, 1997).

As a product of the food chain, plants are also a major source of food for most animals, especially for herbivores. Therefore, ingestion of various media like plants is discussed in the following section on contaminant uptake by animals.

3.2.2 Contaminant Uptake by Animals and Human Beings

For terrestrial animals, contaminant uptake through ingestion is the most important exposure route and has been studied extensively (Brueske et al., 1991; Brummelen and Straalen, 1996; Hunder et al., 1991; Tillitt et al., 1995). Besides oral uptake, dermal and inhalation pathways are also a concern for animal receptors. Recently, contaminant uptake by aquatic animals has received more attention (Hellou et al., 1998; VanVeld, 1998) because contaminants can bioaccumulate in aquatic species, especially in fish resulting in risk to human health by ingestion. Studies have focused for the most part on the uptake mechanisms through direct absorption and oral uptake. Subsequent to uptake, contaminants may undergo absorption, distribution, or excretion. Absorption can occur through the gastrointestinal tract by ingestion, the skin by dermal absorption, and the lungs by inhalation pathways.

Gastrointestinal (GI) Tract (Ingestion)

Toxicants can enter the GI along with food and water by ingestion. The stomach and intestine are the major sites for the absorption and translocation of contaminants in the GI tract. To date, a number of studies have been conducted to help understand the

contaminant uptake mechanisms by ingestion: uptake of planar halogenated hydrocarbons (PHHs) by mink and carp (Tillitt et al., 1995); influence of subchronic exposure to deoxynivalenol (DON), a trichothecene mycotoxin, on intestinal absorption in mice (Hunder et al., 1991); heavy metal uptake by shrews (Brueske et al., 1991); and uptake and elimination of benzo[a]pyrene in the terrestrial *Isopod Porcellio Scaber* (Brummelen and Straalen, 1996). These studies show that numerous factors may be involved with the absorption, which include the nature of the chemical and its matrix, the subject exposed, and the condition of exposure. Among these factors, chemical speciation is critical for understanding absorption and translocation in GI tract. Firstly, pH greatly affects its absorption and, therefore, its toxicity. An example of this phenomenon is provided by aspirin, one of the most common causes of poisoning in humans (Lu, 1996; Manahan, 1989). The chemical name of aspirin is sodium acetylsalicylate. With a pK_a of 3.2, acetylsalicylic acid (HAsc) dominates at a pH substantially below 3.2. This form is easily absorbed by the body, especially in the stomach, where the pH can be as low as 1. Many other contaminants exhibit acid-base behavior and therefore pH is a key factor in their uptake. In addition, pH also affects metal solubility. Typically, to obtain a toxic response, a chemical must be soluble in body fluids or converted to a soluble form in the organ or system through which it is introduced into the body. Insoluble substances are often ingested through the gastrointestinal (GI) tract without doing harm (Lu, 1996), whereas they may be quite toxic if dissolved. For example, barium ion, Ba^{2+}, in the form of insoluble barium sulfate, $BaSO_4$, is routinely used as X-ray-opaque agent in the GI tract for diagnostic purposes. This is a safe procedure; however, soluble barium salts such

as $BaCl_2$ are deadly poisons when introduced into the GI tract (Lu, 1996; Manahan, 1989).

Besides wildlife, humans have been subjects in a number of studies as well. Schlummer et al. (1998) investigated gastrointestinal absorption of polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), and hexachlorobenzene (HCB) from food ingested by seven individuals aged 24 to 81 with varying contaminant exposures. They found that blood lipid levels predominantly controlled the absorption behavior and a good correlation was obtained between the net absorption and the lipid-based concentrations in the blood for almost all of the persistent compounds studied.

As mentioned earlier, the uptake process is influenced by many factors related to contaminants, target receptors, and the environment. Henning et al. (1999) identified exposure factors controlling the uptake of xenobiotic chemicals by colonial piscivorous birds, such as herons and egrets, through the ingestion of fish. These factors, which included feeding rate for various food sources, feeding territory size, and body weight, are critical to the implementation of models commonly used to predict ecological risks. Another important factor influencing dietary uptake is the bioavailability of a chemical in the contaminated matrix such as soil. Ruby et al. (1999) found that the bioavailability of metals like lead and arsenic was mainly controlled by mineralogic soil factors. These factors included contaminant speciation, the relative stability of the compound released to soil, the potential for chemical or physical alteration of this compound, the likely reaction products (based on soil chemistry), and the likelihood of disturbances that may alter soil chemistry.

Skin (Dermal Absorption)

In general, the skin is relatively impermeable, therefore, it constitutes a good barrier, separating the organism from its environment. However, some chemicals can be absorbed through the skin in sufficient quantities to produce systemic effects. Toxicants can enter the skin through epidermal cells, sebaceous gland cells, or hair follicles (Lu, 1996). As a function of both the substance and the skin, permeability also varies with location, temperature, and chemical speciation. In order to penetrate the skin significantly, a substance must be a liquid or gas or significantly soluble in water or organic solvents. In general, nonpolar, lipid-soluble substances traverse the skin more readily than do ionic species. Substances that penetrate the skin easily include lipid-soluble endogenous ones as well as a number of xenobiotic compounds. Breaks in epidermis due to laceration, abrasion, or irritation increase the permeability, as do inflammation and higher degrees of skin hydration.

As a highly lipophilic compound, dermal uptake of benzo[a]pyrene (BaP) was studied by Yang et al. (1989) and Wester et al. (1990). Yang et al. investigated BaP absorption by rats from soil contaminated with crude oil at a concentration of 1% and a BaP concentration of approximately 1 ppm. The study was conducted using rat skin in a diffusion chamber. The average concentrations of BaP absorbed after 96 hours of exposure were 8.4% and 1.3% of the initial applied dose at exposure levels of 9 mg soil/cm^2 of skin and 56 mg soil/cm^2 of skin, respectively.

Roy et al. (1998) studied dermal bioavailability by using polynuclear aromatic hydrocarbon (PAH) contaminated soils. In vitro percutaneous absorption studies were performed with contaminated soils or organic extracts of contaminated soils collected

from a site at a manufactured gas plant (MGP). The PAH concentration in the MGP tar contaminated soils ranged from 10 to 2400 mg/kg, while the concentration in the extracts ranged from 12000 to 34000 mg/kg. Roy et al. measured a 2-3 order of magnitude reduction in PAH absorption through human skin going from the extracts to the most contaminated soil. The results suggested that PAH (or contaminant) sorption on soil could significantly impede their bioavailability to the skin. Unlike the effect of direct contact of PAHs with skin, soil-sorbed PAH must desorb from the solid matrix to the outer layer of the skin prior to penetration and diffusion.

Lungs (Inhalation)

The major function of the lungs is to exchange gases between the blood stream and air in the lungs. Gas exchange occurs in a vast number of alveoli in the lungs, which is the main site of absorption in the respiratory tract. In the alveoli, only one cell separates blood from air. The thin, fragile nature of this tissue makes the lungs especially susceptible to absorption of toxicants and to direct damage from these substances. Furthermore, the respiratory route enables toxicants entering the body to bypass organs that have a screening effect (i.e., the liver). Therefore, these toxicants can enter the bloodstream directly and be transported quickly to receptor sites with minimum intervention by the body's defense mechanisms.

Uptake mechanisms through inhalation have been studied with particle deposition (Harch and Gross, 1964; Hinds, 1982; Lippmann and Schlesinger, 1984; Raabe, 1979; U.S. EPA, 1986) and gas absorption (Fiserova-Bergerova, 1983; Overton and Miller, 1988; U.S. EPA, 1993b). These studies illustrated that for particles, deposition mechanisms include inertial impaction, sedimentation (gravitational), diffusion,

interception, and electrostatic precipitation, whereas mechanisms important for gases include convection, diffusion, chemical reaction (including metabolism), and dissolution. Examples of this type of research include that of Mast et al. (1995), who observed chronic toxicity through inhalation of four types of refractory ceramic fibers in male Fischer rats. Yoshida et al. (1998) considered pharmacokinetics of inhaling 1,1,1-trichloroethane, tetrachloroethylene, trichloroethylene, benzene, and p-dichlorobenzene by male Sprague-Dawley rats. Their research provided relative toxicity data for risk assessment of chronic low-level exposure to chemicals by inhalation.

After uptake through any of the potential pathways, toxicants will undergo distribution and excretion and may cause varying impacts on different tissues as illustrated by Wayland et al. (1999). They evaluated lead concentrations in the liver, kidney, and bone for dead Bald and Golden eagles; results showed that the liver had the greatest body burden among all the tested tissues. Overall, the total contaminant body burdens within the studied terrestrial animals are from ingestion, dermal absorption, and inhalation through the GI tract, skin, and lungs, respectively. Besides terrestrial animals, aquatic animals are important receptors in ecological risk assessment, and they undergo different uptake mechanisms due to their unique aquatic environment.

Direct Absorption for Aquatic Animals

For most aquatic animals such as fish, direct absorption is a major route for the toxicant uptake (Moriaty, 1988; Thomann, 1989). But recent research has shown that in some cases, dietary uptake also plays an important role in the overall exposure of aquatic animals. Van Veld and Vogelbein (1998) studied mummichog (*fundulus heteroclitus*) exposure to aqueous and dietary contaminated BaP. Using immunohistochemical

detection of hydrocarbon-inducible cytochrome P4501A (CYP1A), results showed that both aqueous- and dietary-borne contaminants contribute towards overall exposure. However, they also noted that these processes are strongly influenced by the complexity of biogeochemical cycling of toxicants, species differences, temporal factors, trophic levels, feeding strategies, composition of food, lipid content of fish, sex, season, binding of toxicant to dissolved organic matter in water, complex mixtures of toxicants, and multiple synergistic and antagonistic effects.

Hellou et al. (1998) compared the dietary and aqueous exposure of yellowtail flounder to organochlorine compounds. They found that levels of contaminants were three to 20 times greater from the aqueous partitioning as compared to the dietary uptake for inshore flounder that fed on organochlorine compounds contaminated capelin, *mallotus villosus*, for 2 years. This comparison suggests a major influence of inshore water on the bioaccumulation of contaminants, although the effect of altering the diet of flounder cannot be disregarded. Kraal et al. (1995), however, found different results from studying the uptake and tissue distribution of dietary versus aqueous exposure to cadmium by carp. In their laboratory experiments, the fish were exposed to Cd-contaminated food or water for 4 weeks. The Cd accumulation in the tissues of fish fed contaminated larvae was observed to follow the order of gut > kidney > liver = gill > muscle, while exposure to contaminated water resulted in gut>gill>kidney>liver>muscle. In almost all tissues, the Cd concentrations were similar regardless of the route of exposure; only the gill had accumulated more Cd from contaminated water than from food. These findings suggested that uptake of Cd from contaminated prey (or food) plays an important role in aquatic ecotoxicology. Thomann et al. (1992) found that dietary

uptake of organic contaminants is the most significant route of exposure and bioaccumulation for contaminants with K_{ow} greater than approximately 10^5-10^6. On the other hand, for chemicals with a K_{ow} less than 10^5, chemical uptake from the water is usually the most significant pathway (Clark et al., 1990)

Since biomagnification of organic contaminants in food chains has been observed in laboratory and field studies, it is important to understand the mechanism by which contaminants are absorbed and concentrated in assessing environmental risk. One of the first mechanistic explanations for bioaccumulation was based on biomass-to-energy conversion (Woodwell, 1967). Unable to reproduce the observations of Woodwell, Hamelink (1971) proposed that bioaccumulation in aquatic food chains is due to a physical-chemical partitioning (or bioconcentration) of the chemical between the water and the organism. Gobas et al. (1999) further investigated fugacity of hydrophobic organic contaminants in the GI tract of fish under controlled laboratory and field conditions. The findings indicated that food digestibility and absorption are critical factors controlling biomagnification. Although their study was conducted with fish, it is expected that the dietary uptake process applies to many organisms.

3.2.3 Summary

The discussed studies illustrated the uptake mechanisms for plants and animals. The uptake process can be very complicated and may involve numerous factors associated with the chemical and the receptors. However, potential limitations are associated with laboratory studies. For example, only single stressor is concerned and multiple stressors study can be limited by cost and logistical considerations; non-measurable effects (i.e.

weather effect) are not included under the fixed laboratory condition. Those limitations can bring big gap between approach in the lab and the approach to exposure in the fields. Therefore, the extrapolation of laboratory data to the field study has to be addressed with uncertainty analysis.

Compared with empirical measurements in the discussed studies above, exposure models for estimating uptake of chemical contaminants through direct exposure to contaminated media and secondary exposure to contaminants present in the food web can be a cost effective method to identify concerned areas. However, considering that some critical factors influencing chemical uptake, for example, speciation, are complex and not necessarily reflected in the mathematical models, an ecological risk assessment cannot produce absolute answers regarding exposure where uncertainty must be addressed.

3.3 Exposure Model

Based on the literature reviewed (Hope, 1995; U.S.EPA, 1993; Cheng, 1998; PNNL, 1998), quantitative exposure estimations to predict contaminant uptake were identified for the ERA model. Each mathematical equation for exposure incorporates species-specific information on diet composition, body weight, home range, food and water ingestion rates, and incidental ingestion rates of environmental media, as available (Appendix A).

3.3.1 Exposure Pathways and Food Web

The general exposure pathways are listed in Table 11; given these, the equations can be combined to produce site- and species- specific estimation of chemical uptake from

abiotic and biotic media. These various routes of exposure and the key information required to estimate these exposures are shown in Figure 26. The hierarchical nature of exposure is depicted in Figure 26 by three levels of foraging life styles. The body burden of plants is based on uptake of contaminants from air, soil, pore water, and groundwater. Uptake may be either through the roots or through transport across above ground membranes containing aerial deposits of vapor-phase contaminants. Herbivores and omnivores consume this plant material along with the contaminants that have been deposited on the plant tissues as particulate matter. They may also ingest soil directly, and all consume water, which may itself contain contaminants. Omnivores and carnivores consume animal prey that has also received some degree of exposure. Besides the level of contamination present in the various pathways of exposure, the fractional absorption of these contaminants controls both the resulting concentrations in the organism and its toxicological response to those absorbed concentrations. The predator-prey food web is relationally imbedded within the database structure. This method allows any number of organisms to be included without increasing the mathematical complexity. The approach involves deriving a general expression for uptake and clearance of a chemical by a single organism, and applying a set of such expressions that can be easily manipulated in a relational database. Compared with a matrix structure method introduced by Steven et al (2000), the trophic levels expressed in a relational database are more flexible and easily modified for a specific food web. Furthermore, a DBMS approach is not restricted to one

Table 11 Exposure Routes for Different Receptors

Target Receptor	Exposure Route	Exposure Point
Terrestrial Plants	Root Uptake	roots in contact with root-zone soil (~1m depth)
		roots in contact with soil solution (surface water or ground water)
		translocation to above-ground plant parts from roots in contact with root-zone soil (~1m depth)
	Foliar Uptake (dust)	foliar or stem contact with gas-phase contaminant volatilized from soil
	Foliar Uptake (vapor)	deposition of particulate-bound contaminants on plant surfaces (leaves and stems)
Terrestrial Animals	Dermal Contact	direct exposure to surface water, soil and /or exposed sediments
	Inhalation (dust)	inhalation of particulate-bound contaminants while foraging in soil and/or exposed sediment
	Inhalation (vapor)	inhalation while in burrow of gas-phase contaminants released from soil and /or exposed sediment
	Ingestion	incidental ingestion of soil and /or exposed sediment; ingestion of surface water; ingestion of contaminated forage/prey
Aquatic Plants	Direct Contact	osmotic equilibrium with surrounding surface waters
Aquatic Animals	Direct Contact	respiration, ventilation, or osmotic equilibrium with surrounding surface or pore waters
	Ingestion	regular or incidental ingestion of sediment; ingestion of contaminated forage/prey

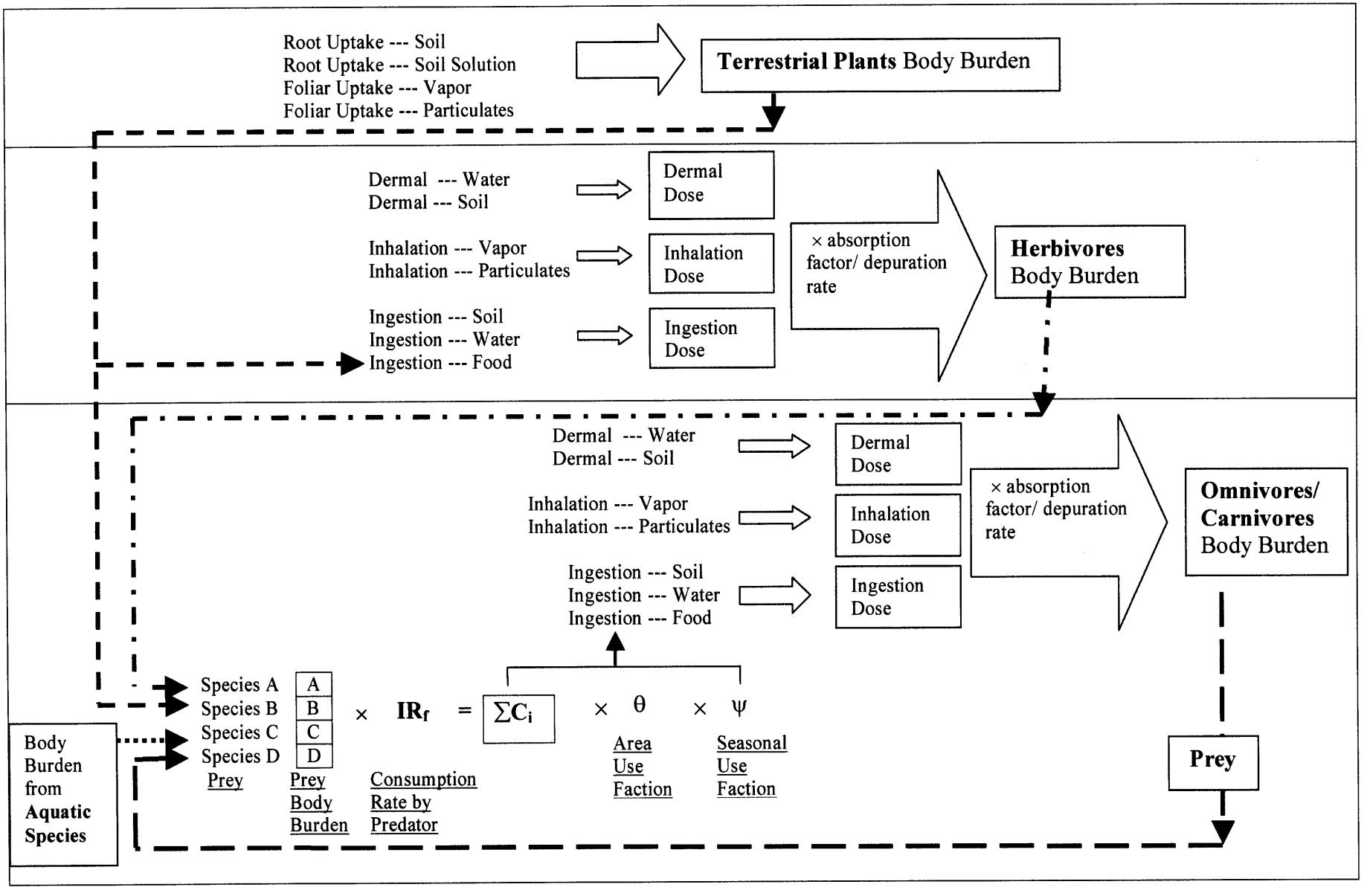

Figure 26 Conceptual Model (PNNL, 1998)

receptor per species. The exposure algorithms applied to the ERA model are described in the following sections.

3.3.2 Terrestrial Plants Exposure

Plants are receptors for contaminants and subsequently stressors in the food chain. Therefore, calculating contaminant concentration in plant tissue is a necessity. Uptake of contaminants by plants is a complex process that involves processes such as adsorption, complexation, and precipitation (Farago, 1994; Ross, 1994). However, an approach based on plant-soil (K_{ps}), plant-soil solution (K_{pw}), and plant-air (K_{pa}) partition coefficients can provide a simple and useful method for assessing uptake and risk. For the three exposure pathways, Equation (3.1) is applied:

$$C_i = EC_i \times K_{pi} \tag{3.1}$$

$$C_{total} = \Sigma C_i \tag{3.2}$$

where

C_i = contaminant concentration in receptor from the i^{th} pathway (mg/kg)

C_{total} = total contaminant concentration in receptor from exposure to soil, water and air (mg/kg)

EC_i = contaminant concentration in medium (mg/kg for soil EC_s, mg/L for water EC_w, and mg/ m^3 for air EC_a)

K_{pi} = plant-medium partition coefficient ([mg/kg] soil / [mg/kg] roots for plant-soil – K_{ps}, L/kg for plant-solution -- K_{pw}, and m^3/kg for plant-air K_{pa})

In the event a partition coefficient is not available, it can be estimated. For organics, the coefficient is determined from the octanol-water partition coefficient (K_{ow}) (Lyman et al., 1990). For inorganics, the geometric mean of bioconcentration factors for leafy and root vegetables can be applied to represent above ground and below ground plants, respectively (Hope, 1995; Strenge and Peterson, 1989). As a result of these estimation methods, this approach may under estimate the final risk to the plants. In model validation (chapter 5), the effect of these estimation methods will be addressed.

3.3.3 Terrestrial Animals Exposure

Ingestion, inhalation, and dermal absorption present the principal means by which terrestrial wildlife receptors are exposed to contamination. As mentioned above, these receptors may receive exposure through direct contact (primary pathway) with abiotic media and consumption (secondary pathway) of contaminated food. Exposure estimation for these species must, therefore, include consideration of contaminant body burdens in the lower trophic level forage or prey based on the food web. Because using a food web model requires ecological information with respect to historical data and site-specific feeding relationships, the process introduces a crucial ecological perspective into what might otherwise be a purely toxicological exercise (Hope, 1995).

Dermal exposure could be a significant exposure route for animals that are in frequent contact with contaminated water, sediment, or soil. But the estimation of contaminant uptake via dermal absorption is also problematic for ecological resources, primarily because many of the required parameters have not been measured for terrestrial biota (U.S. EPA, 1993). The following model (U.S. EPA, 1993) is developed to estimate

exposure based on an approximation of the mass of soil or sediment adhering to an area of an animal's skin surface.

$$ADD_i = [(SA \times AF \times P_{cs} \times EC_s \times CF \times \alpha_i)/BW] \times \theta \times \psi \quad (3.3)$$

$$C_i = ADD_i / k_e \quad (3.4)$$

where

ADD_i = applied daily dose to the receptor through the i^{th} exposure pathway (mg contaminant/kg of receptor body weight)

SA = surface area of ecological receptor (cm^2)

AF = soil-to-skin adherence factor (mg/ cm^2)

P_{cs} = fraction of receptor surface area in contact with soil per day (d^{-1})

α_i = contaminant-specific absorption factor (mg/kg contaminant body burden / mg/kg absorbed daily dose)

k_e = contaminant-specific depuration rate (d^{-1})

BW = body weight of receptor (kg)

CF = conversion factor (1×10^{-6} kg/mg)

θ = site use factor

ψ = seasonality factor; percentage of time per year receptor dwells at site

Exposure via inhalation of volatilized contaminants and fugitive dust is evaluated with the following equation (U.S. EPA, 1993):

$$ADD_i = [(IR_a \times EC_a)/BW] \times \theta \times \psi \quad (3.5)$$

$$C_i = ADD_i \times (\alpha_i / k_e) \quad (3.6)$$

where

IR_a = inhalation rate (m^3/day)

Ingestion of contaminants is typically the most significant route of exposure in assessing risks to terrestrial animals. In terms of both frequency and magnitude, for receptors above the primary producer trophic level, ingestion can include both secondary exposure, where contaminated forage or prey is consumed, and primary exposure, where contaminated water, sediments, or soil are consumed. The associated algorithms are

$$ADD_i = [(EC_s \times FS \times IR_i) / BW] \times \theta \times \psi \quad (3.7)$$

$$ADD_i = [(EC_i \times IR_{iw})/BW] \times \theta \times \psi \quad (3.8)$$

$$ADD_i = \sum (C_k \times FR_{fk} \times IR_i/BW) \times \theta \times \psi \quad (3.9)$$

where

FS = mass fraction of soil or sediment in the diet (as percentage of diet on dry weight basis)

IR_i = ingestion rate on dry-weight basis (kg/day)

IR_{iw} = ingestion rate of drinking water (mg/day)

FR_{fk} = wet weight fraction of the k^{th} food item in receptor diet (kg food/kg diet)

For the total applied daily dose per terrestrial animal from all the above exposure pathways:

$$ADD_{total} = \Sigma ADD_i \quad (3.10)$$

where:

ADD_{total} = applied daily dose through all the concerned exposure pathways (dermal absorption, ingestion and inhalation) (mg contaminant/kg of receptor body weight)

Equations (3.7 – 3.10) are derived from the Wildlife Exposure Factors Handbook (U.S. EPA, 1993) and Hope (1995) and are applied to wildlife ingestion of contaminated soil, water, and food. The exposure parameters were obtained from literature (Owen, 1990; Maughan, 1993;) and government databases, for example, ECOTOX (U.S. EPA, 2000) and MEPAS (Strenge et al., 1989), or estimated with empirical equations recommended by for example, the U.S. EPA (1993). Appendix A illustrates the detailed derivation of the equations and parameters.

3.3.4 Aquatic Species Exposure

Aquatic species are the target receptors exposed to the contaminants in the aquatic systems such as surface water. In the ERA model, they are defined as non-rooted, free-floating aquatic macrophytes and free-swimming aquatic animals. Total uptake for these species is represented by partitioning from surface water (Hope, 1995).

$$C_{aq} = EC_{sw} \times BCF \quad (3.11)$$

where

C_{aq} = contaminant body burden in aquatic receptor (mg/kg)

BCF = contaminant-specific bioconcentration factor (L/kg)

The contaminant-specific BCF can be obtained from the literature (Lyman, 1993; U.S. EPA, 2000). Factors not available for inorganic contaminants (e.g., metals) may be estimated from empirical equations using the species solubility constant (K_{so} mg/L) (Sample et al., 1996) (see appendix A and B).

As indicated in the previous section, generally, exposure for aquatic receptors will be dominated by bioconcentration (direct uptake from water) mechanisms as opposed to bioaccumulation (uptake through food and water assumption) mechanisms unless the contaminant has a log (BCF) greater than 5 (Thomann, 1989; Moriaty, 1988). Considering the lack of data on aquatic animal uptake through ingestion, this model only includes direct absorption for aquatic animals.

Generated from literature review (Hope, 1995) and U.S. EPA recommendations (U.S. EPA, 1993), the exposure models cover potential exposure pathways for terrestrial and aquatic animals and plants. They have been adopted or modified to implement ecological risk assessment case studies (Sample et al., 1994; PNNL, 1998; Kester et al., 1998; Hope 1999; Pascoe et al., 1999; Dwayne et al., 1999). In the East Fork Poplar Creek case study, Dwayne et al. (1999) modified the ingestion exposure model by using an exposure-reduction factor to address the mercury and PCBs exposure to mink and kingfishers. To address the influence of surface water concentration reduction on the risk evaluation, the assessors assumed that these reduction would lead to a proportional decrease in the body burden concentrations of aquatic prey. However, this assumption may be quite suspect if the environmental conditions controlling methylation rates,

bioaccumulation of mercury (i.e., pH, redox potential and temperature) and bioavailabiltiy and bioaccumulation of PCBs (i.e., levels of dissolved organic matter) changes. Furthermore, this approach is applied only to surface water concentrations and tissue levels in aquatic prey (fish and invertebrates) because reductions in mercury or PCBs aquatic concentrations would not affect other exposure pathways. Therefore, the specific case study condition has to be reviewed for modification of these exposure models.

The estimate methods and conditions associated with the applied parameters have been discussed in detail in Section 3.4 of the *Wildlife Exposure Factors Handbook* (USEPA, 1993). Among them, estimate of seasonality factor and site use factor can vary significantly based on different site conditions and receptor's life history. Therefore, the availability of comprehensive information on sites and receptors can be critical factor for reducing the uncertainty associated with such parameters.

These exposure models for terrestrial and aquatic plants and animals are applied in software developed using Visual Basic 6.0 with associated parameters stored in the Microsoft SQL Server DBMS. A detailed description of the model and parameters is provided in Appendices A and B.

3.4 Risk Characterization

Once the ecosystem and site characteristics are fully understood and the applied daily dose (ADD) or body burden can be estimated for an individual receptor, an ecological hazard quotient (EHQ) is calculated by dividing the ADD (or body burden) by the reference values (Weiss, 1999):

$$EHQ = ADD_{Total} \div \text{Reference Value} \quad (3.12)$$

Reference value recommended in this model is the no observed adverse effect level (NOAEL) or no observed adverse effect concentration (NOAEC) for terrestrial and aquatic species, respectively. NOAEL and NOAEC are derived from experiments conducted on laboratory animals, and are the highest dose applied or contaminant concentration that did not result in a measurable adverse effect (Cockerham et al., 1994). This is the most conservative approach (Bascietto et al., 1990), and is the one used in the RESRAD Ecorisk model (Cheng, 1998) and CRCIA (PNNL, 1998). However, disagreements exist on the NOAEL (or NOAEC) application partly because of its estimator of "safe" chemical concentrations (Crane et al., 2000). Moreover, toxicity data are limited for wildlife; consequently, NOAELs are often estimated from laboratory studies and by extrapolating toxicity data such as LD_{50} values for domestic or laboratory animals to wildlife (Sample et al., 1996).

Extrapolation of toxicity data immediately introduces uncertainty into any model. As a general rule, organisms with smaller bodies have a tendency to detoxify faster than larger ones, because of their higher metabolisms; however, there are exceptions (Sample et al., 1996). If for example, the toxic effect is produced by a primary metabolite, the detoxification process may be disrupted (Sample et al., 1996). Generally, because smaller animals have a tendency to detoxify quicker (i.e., mice), application of data to larger animals (i.e., deer) may significantly underestimate a risk. Correcting for body weight and varying metabolic rates, wildlife NOAELs can be estimated for an untested species by the following equation (Sample et al., 1996):

$$NOAEL_{wildlife} = NOAEL_{test}\left(\frac{bw_{test}}{bw_{wildlife}}\right)^{0.25} \quad (3.13)$$

where the $NOAEL_{wildlife}$ represents the ecosystem receptor of concern, the $NOAEL_{test}$ is the surrogate test species for which the NOAEL is available, and *bw* represents their respective body weights (Sample et al.,1996; EPA,1993). The (0.25) exponent is a scaling factor used to account for the physiological functions of different species' metabolic rates, and was obtained empirically by Sample et al. (1996). The algorithm that Sample et al. (1996) apply to calculate the NOAELs for wildlife avian species defaults to a body weight ratio raised to a zero exponent, based on empirical relationships resulting from tests conducted on birds using LC_{50} data for 37 pesticides. Avian body weights did not vary significantly, therefore, Sample et al. (1996) concluded that zero is the most appropriate scaling factor for interspecies extrapolation between birds.

When NOAELs (or NOAECs) are not available for the target or laboratory receptors, they can be estimated based on the lowest observed adverse effect level (LOAEL or LOAEC) or Lethal dose (LD_{50} or LC_{50}) by applying an uncertainty factor (Sample et al., 1996 and 1998):

$$\text{NOAEL (or NOAEC)} = \text{LOAEL (or LOAEC)} / 10 \quad (3.14)$$

$$\text{LOAEL (or LOAEC)} = LD_{50} \text{ (or } LC_{50}) / 15 \quad (3.15)$$

The application of uncertainty factor s of 10 and 15 are demonstrated by Sample et al. (1996) and consistent with U.S. EPA guidance (EPA, 1997).

NOAEL (or NOAEC) stored in the Microsoft SQL Server DBMS of the model are gathered from the toxicological benchmarks database for terrestrial animals and plants prepared by Oak Ridge National Laboratory (Sample et al., 1996; Efroymson, 1997), the

Ecotox database of U.S. EPA (2000), and MEPAS database of PNNL (1998). Toxicity studies were conducted on a variety of chemical species to obtain these data (Sample et al., 1996; Efroymson, 1997). Particular endpoints are associated with the benchmark measurements. In this model, morality was evaluated for aquatic receptors and plant growth or yield for terrestrial plants. As terrestrial animals concerned, available studies on wildlife or laboratory species may not include evaluations of all significant endpoints for determining long-term effects on natural population. Important endpoints such as reproductive and developmental toxicity and reduced survival were used whenever possible in the model; however, for some contaminants, limitations on the available data necessitated the use of endpoints such as organ-specific effects. It should be emphasized that in such case the resulting NOAELs (or NOAECs) represent conservation values whose relationships to potential population level effects are uncertain. These values need to be recalculated if and when more appropriate toxicity data become available (Sample et al., 1996 and 1997).

Based on the selected reference values, the different range of EHQ values present different level of risk. To be ecologically protective, the ratio of the exposure to the NOAEL (or NOAEC) should be less than 1, because this provides a reasonable level of assurance that an adverse effect would not occur as a result of exposure (U.S. EPA, 1993; Kubiak et al., 1991). An EHQ greater than 1 indicates an adverse risk and less than 1 indicates a potential but non-adverse risk (Table 12). The risk is involved with the potential endpoints for the evaluated ecological system, including effects on

Table 12 EHQ Risk Characterization

EHQ Value Range	Risk Characterization
<1.0	Potential risk to receptor
1.0 - 10.0	Slight potential adverse risk to receptor
10.0 - 100.0	Moderately high potential adverse risk to receptor
> 100.0	Extreme adverse risk to receptor

reproduction, development, and organ-specific toxic effects (i.e., liver or kidney damage) (Sample et al., 1996). As discussed earlier in this section, 10 × the NOAEL (or NOAEC) is approximately the LOAEL (or LOAEC), which means the lowest dose applied (or contaminant concentration) that will result in a measurable adverse effect. Therefore, for reasonable maximum exposure scenarios, EHQ values between 1 and 10 suggest that the ADD (or body burden) is greater than the NOAEL (or NOAEC) but less than the LOAEL (or LOAEC). However, for most exposure scenarios, if an EHQ greater than 10, the ADD (body burden) is greater than the LOAEL (or LOAEC), and the exposure to the contaminants could result in an adverse effect on the receptor's reproduction, development, natural population, or organ-specific responses. Consequently, the range of 10–100 is generally considered to represent a significant ecological risk (U.S. EPA, 1993). Also, based on the previous extrapolation of NOAEL (or NOAEC) from LD_{50} (or LC_{50}), an EHQ value greater than 100 indicates that the contaminant uptake is generally greater than the lethal dose which represents death of 50% of a test population. The associated risk is recognized as the extreme adverse one. Based on such a categorization, the adverse risk is divided into three levels in this model (U.S. EPA, 1993; Cheng, 1998):

between 1 and 10, a slight potential adverse risk exists; greater than 10 but less than 100 indicates a moderately high potential risk; and greater than 100 is an extreme adverse risk (Table 12).

As discussed in Chapter 3, contaminant speciation determines how it will be absorbed and excreted. For example, organometalic compounds because of their lipid solubility have a tendency to remain in the body longer than inorganic ones. The resulting EHQ may not accurately represent the actual contaminant behavior.

3.5 ERA Software Development and Testing

These exposure models for terrestrial and aquatic plants and animals with respect to the application of EHQ for the risk characterization are integrated into the ERA software developed using Visual Basic 6.0 with associated parameters stored in the Microsoft SQL Server DBMS. Based on criteria that included using personal computers, programming language compatibility, user-friendliness, and storage volume for data, Visual Basic 6.0 and Microsoft SQL Server were selected for developing the interface and local DBMS.

The DBMS stores data required for conducting ecological risk assessments. These data include inorganic and organic contaminants, site characteristics, chemical properties, receptors, algorithm parameters, and reference values (Strenge, 1989; Owen, 1990; Lyman, 1990; Hope, 1995; Sample, 1996; U.S. EPA, 1993, 1998; Cheng, 1998). With guidance included in the software, these data can be modified to satisfy site-specific conditions. Furthermore, the local DBMS will be linked with external ones including the U.S. EPA Ecotox (U.S. EPA, 2000) to resolve timely data needs. The structure of the ERA software is illustrated by Figure 27.

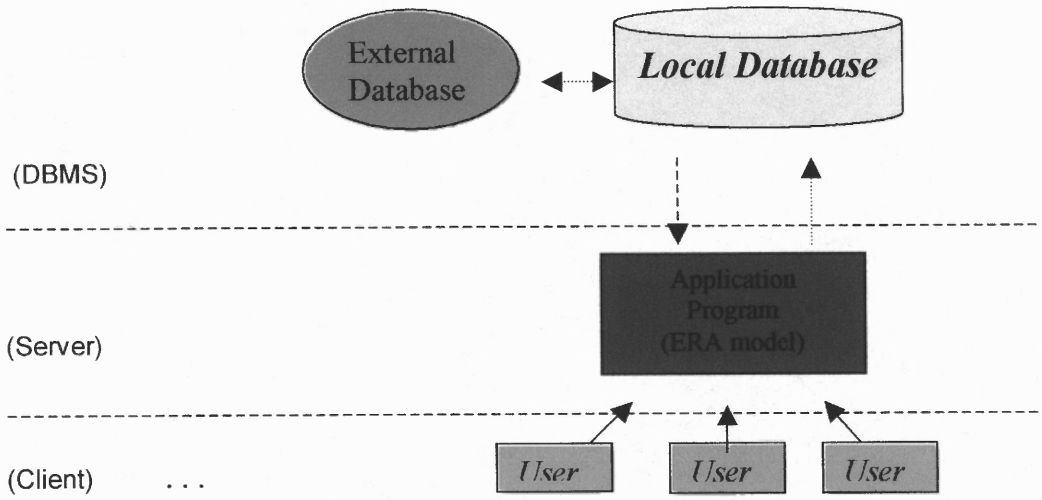

Figure 27 ERA Software Structure

Prior to implementing the case study, the model was tested for logic and meaningfulness. A range of hexavalent chromium concentrations in different media (1-10 mg/L for surface water; 100-1000 mg/kg for soil; 0.1-1 mg/m^3 for air) was selected to assess exposure to terrestrial and aquatic receptors. The contaminant uptake (ADDs or body burden) as functions of concentration is plotted in Figures 28-33. Figures 28 and 29 illustrate the linear relationship between chromium concentration in surface water (environmental concentration -- EC_{sw}) and in aquatic receptors, mountain whitefish and the periphery plant. Similarly, for the terrestrial red fox receptor, the change in ADDs with the increase of chromium concentration in air (EC_a), soil (EC_s), and drinking water (EC_w) are presented in Figures 30 - 32. Figure 33 illustrates the relationship between the body burden and EC_s for the terrestrial plant rushes. From these figures (28-33), we can see that with an increase in concentration, the chromium uptake (ADDs or body burden) increase linearly with no outliers. Such results demonstrate that as contaminant

concentration in a medium increases, the body burden or applied daily dose increases proportionally as would be expected given the associated algorithms shown in Chapter 3.3. Therefore, as the media concentration increases, the risk to the ecosystem rises.

3.6 Summary

Based on ecosystems defined in Chapter 2, the potential exposure pathways were identified to include ingestion, inhalation, and dermal absorption for terrestrial animals; root and foliar uptake for plants; and direct absorption for aquatic species. From the laboratory and field studies, numerous factors associated with the properties of chemicals and receptors and the exposure conditions are involved in the uptake mechanisms for plants and animal. Since uptake and exposure are complicated, simplifications in the analyses are conservative and cost-effective. Therefore, the exposure can be estimated from the available data by an ecorisk model if it is carefully applied. In the model developed, the ecorisk algorithms cover all exposure pathways and risk is characterized by comparing the estimated contaminant uptake by a receptor to the NOAEL or NOAEC, which is defined as EHQ. To apply a complex food web, the trophic levels are considered and evaluated through the relational DBMS to express predator-prey food relationships in the model. The ERA code is written in Visual Basic and integrated into the software by linking it with a Windows-based interface and the DBMS. The developed ERA software was subsequently verified. However, as a simulation tool, ecorisk models cannot reflect natural uptake processes. For example, these models do not account for the influence of synergistic effects from multiple stressors. Such a limitation introduces additional uncertainty to the final result and needs to be further addressed.

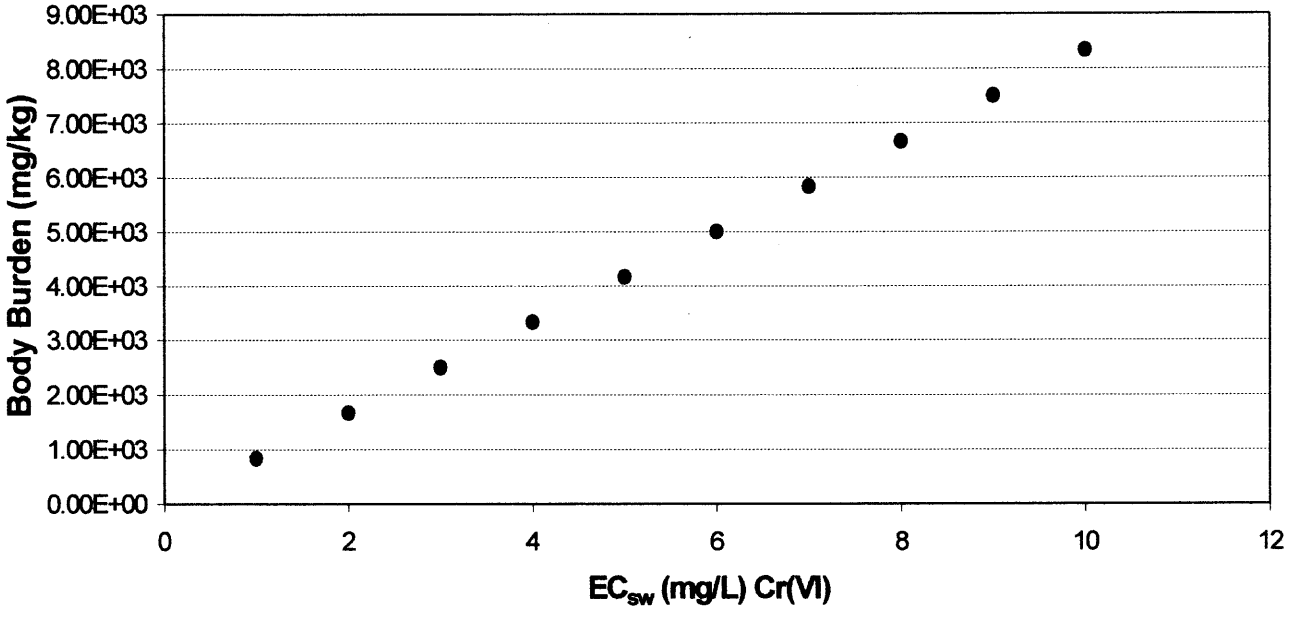

Figure 28 Cr[VI] Body Burden vs.ECsw for Mountain Whitefish

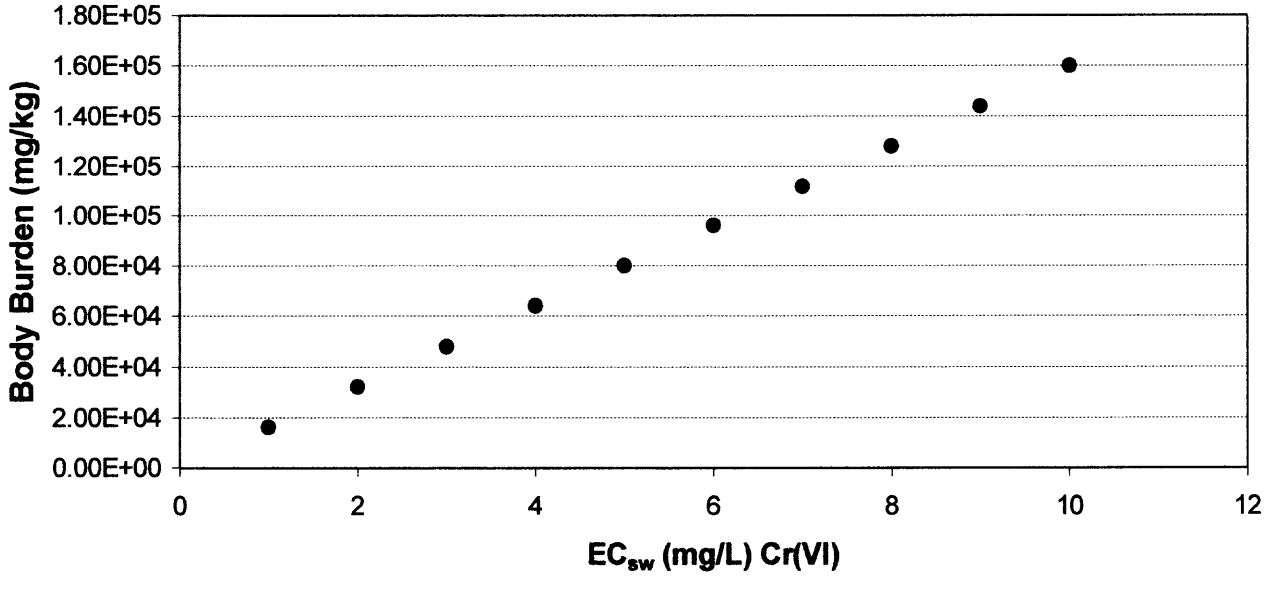

Figure 29 Cr[VI] Body Burden vs. ECsw for Periphyton

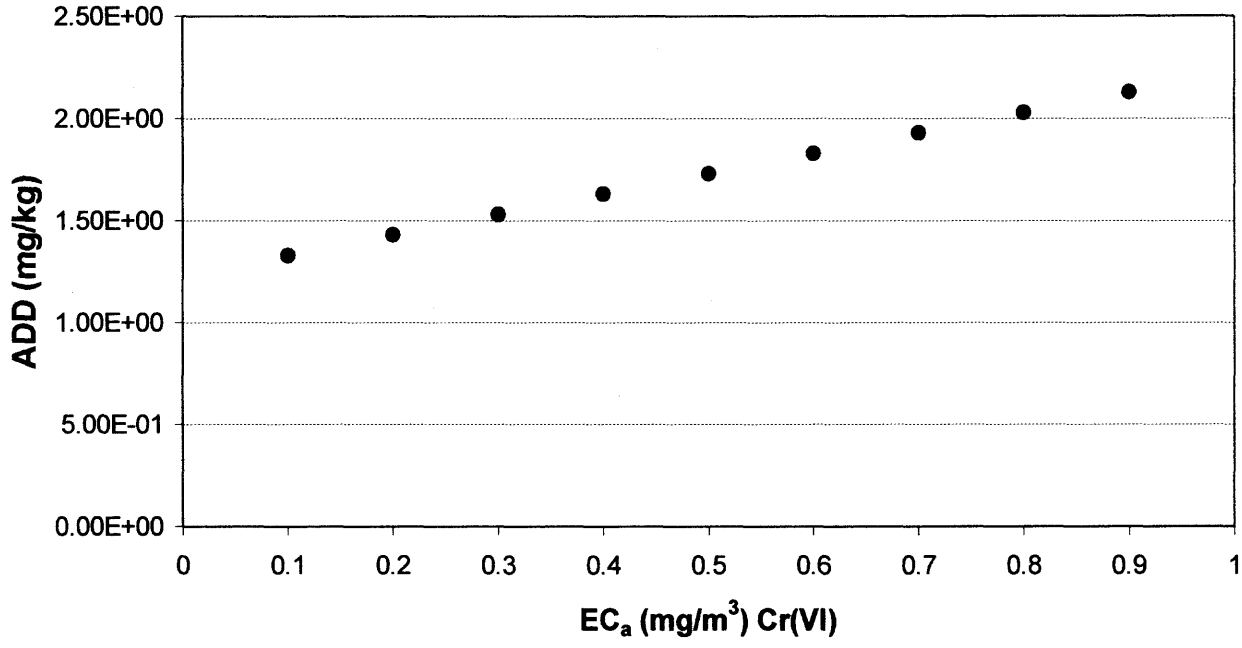

Figure 30 Cr[VI] ADDs vs. ECa for Red Fox

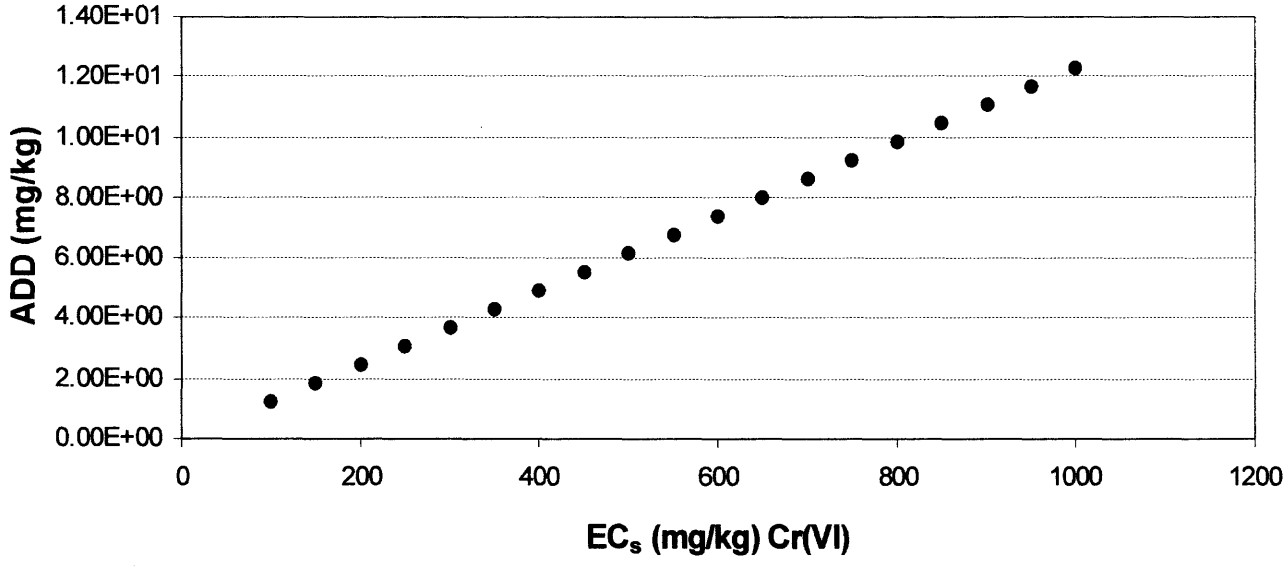

Figure 31 Cr[VI] ADDs vs. Ecs for Red Fox

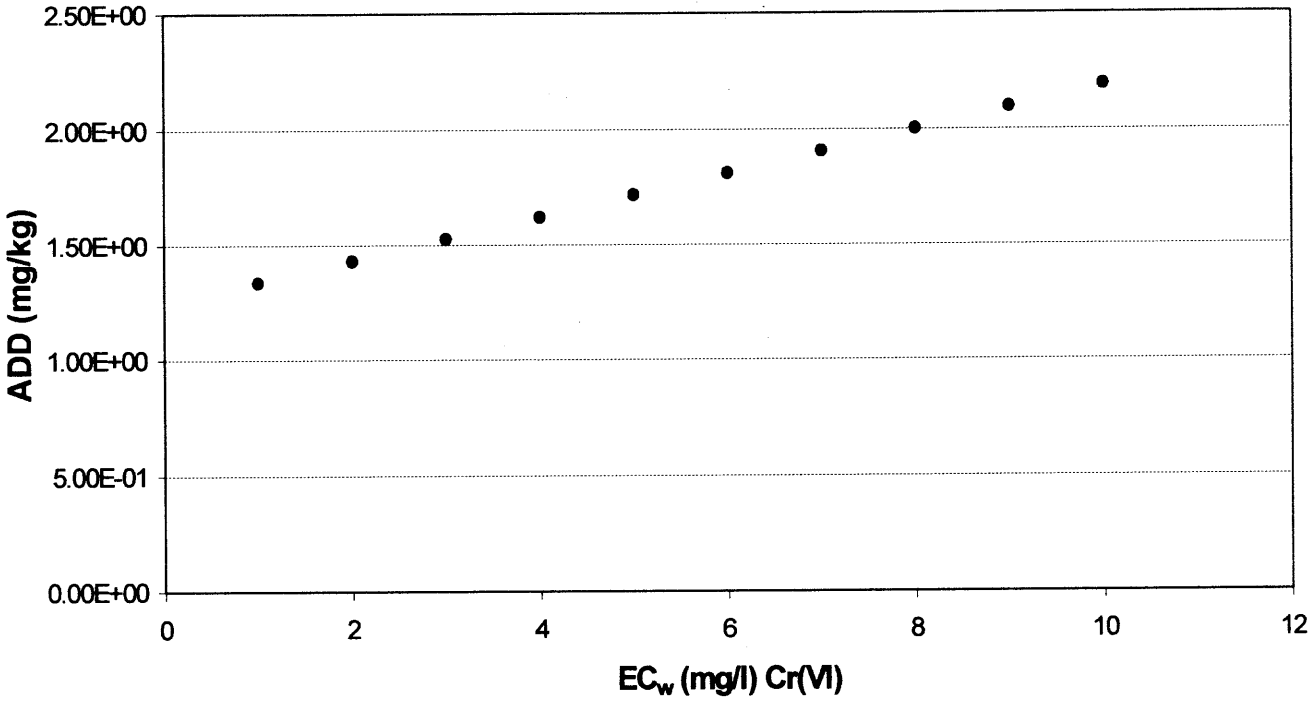

Figure 32 Cr[VI] ADDs vs. ECw for Red Fox

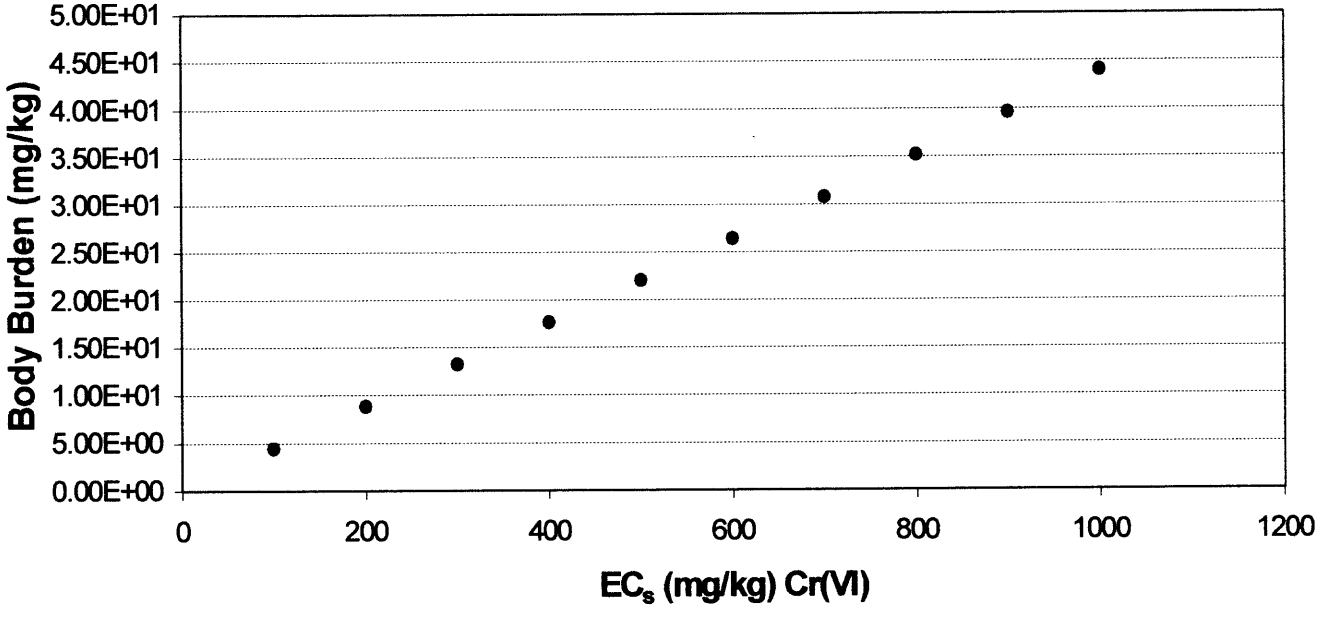

Figure 33 Cr[VI] Body Burden vs. ECs for Rushes

CHAPTER 4

CASE STUDY

4.1 Introduction

In the first stage of the research, Yuma and Aberdeen Proving Grounds were selected as baseline ecosystems for the case study representing an arid desert system and a coastal environment, respectively. Terrestrial and aquatic plant and animal receptors and site characteristics were assembled based on guidelines for conducting an ecological risk assessment (ERA) (U.S. EPA, 1998). The most important routes of exposure at YPG are root uptake for terrestrial plants and ingestion, inhalation, and dermal absorption for the terrestrial animals. All potential routes of exposure are considered for terrestrial and aquatic species at APG, which includes root uptake for terrestrial plants; ingestion, inhalation, and dermal absorption for terrestrial animals; and direct contact for aquatic species. In applying the case study of evaluating the effect of replacing hexavalent chromium with sputtered tantalum, hexavalent chromium and tantalum concentrations in the media must be defined based on use, release, storage, and transport of the processed gun barrels. Other than tantalum, molybdenum is also another alternative coating to replace chromium and is evaluated in the case study.

In this chapter, the case study is implemented based on the developed ERA model. The input data are discussed, which includes the rationale for selected contaminant concentrations, distribution coefficients, and bioconcentration factors. Risk characterization is conducted for the case study examining the two ecosystems, and results are analyzed.

4.2 Exposure Point Concentration

The 95% upper confidence limit (UCL) is calculated as the exposure point concentration based on the mean of the actual, modeled, or estimated contaminant concentration in each medium.

$$95\%\,UCL = X + t\,(s/\sqrt{n}) \tag{4.1}$$

where:

X = arithmetic mean;

t = one-tailed t-statistic value with n-1 degrees of freedom and a significance level of $P < 0.05$;

s = arithmetic standard deviation of the characterization data; and

n = is the sample size.

The use of the 95% UCL as the exposure point concentration is consistent with U.S.EPA Region III guidance for conducting ecological risk assessments (Davis, 1994). This concentration serves as an estimate of the reasonable maximum exposure (RME), which is defined as potentially the maximum exposure that is expected to occur at a site (U.S. EPA, 1989). The calculated 95% UCL value has been used as the RME exposure point concentration for modeling contaminant uptake with the following exception. If the value is less than the maximum concentration, then the maximum reported concentration is used.

Compared with hexavalent chromium, trivalent chromium is sparingly soluble and less toxic, and long term studies of exposures to low levels of chromium in animals have not resulted in any adverse health effects (Sullivan et al., 1992; Finley et al., 1996;

Vajpayee et al., 2000). Therefore, trivalent chromium is not included in the case study. The maximum reported concentrations (> 95% UCL value) for chromium are used for hexavalent chromium based on soil and air sampling data conducted at YPG (U.S. Army YPG, 1999). Therefore, assuming test firing continues at the same rate and the loss of a replacement metal is equivalent to that of the chromium, equivalent concentrations have been used for the alternative metal coating Ta and Mo as well (Appendix D). For APG, no data were available. However, as YPG has a greater gun barrel testing capability and longer testing history than APG and considering a worst-case scenario, the concentrations observed at YPG have been applied to APG. Contaminant speciation used in this effort is listed in Appendix D. The resulting chromium concentrations in each medium for both sites are listed in Table 13. Based on the contaminant concentration in soil, the concentration in surface water of APG was estimated using soil-water distribution coefficients, which is a function of the type of soil as well as solution conditions. Soil water distribution coefficients are discussed in the following section.

Table 13 Chromium (VI) Media Concentrations in APG and YPG

Sites	Soil–phase concentration EC_s (mg/kg)	Soil to water distribution coefficient[b] K_d (cm^3/g)	Surface water concentration E_{sw} (mg/L)	Particulate air concentration EC_a (mg/m^3)
YPG	7.5[a]	70	0.107	1.9E-6[a]
APG	7.5	1500	0.005	1.9E-6

[a] Data from Field Investigation Report of YPG (U.S. Army YPG, 1999)
[b] Source: Yu et al. (1993)

4.3 Soil-water Distribution Coefficients

As discussed in the last section, when no data on contaminant concentrations in surface water are available, soil water distribution coefficients (K_d) can be used for estimating these. In the future, however, when the ERA model is linked to a transport model, the ability to describe contaminant distribution mechanisms will be important for assessing long-term risks. As a result, parameters, like that of the K_d, will have a potentially significant role in the model development. The distribution coefficient represents the partitioning behavior of the solute between the soil and bulk aqueous phase, assuming equilibrium. The K_d values strongly depend on the physical and chemical characteristics of the soil, which in themselves, do not necessarily remain constant over the long-term because soils are dynamic systems. Soil properties that affect distribution mechanisms include mineralogy, the organic matter, pH, and the presence of competing species for the soil surfaces and complexing agents. Applying distribution coefficients assumes that kinetically limited processes are insignificant, which is not true (Bethke and Brady, 2000; Trivedi and Axe, 1999, 2000). Such processes include but are not limited to slow sorption observed as surface precipitation, solid solution formation, and surface diffusion in microporous minerals.

The distribution coefficient can range over several orders of magnitude under varying conditions (e.g., pH) and may result in significant uncertainty when for example, equilibrium does not exist and values are assumed constant throughout the site and as a function of time. In this case study, the soils at YPG are characterized as sandy soil with slow infiltration rates and high runoff potential; however, this potential is generally poor because of low precipitation. The soil pH ranges form 7.4 to 8.4. A K_d of 70 cm^3/g for

sandy soil has been selected for YPG (Table 13) (Yu et al., 1993). Soils in APG are underlain by loamy, gravelly, or clayey sediments on smooth uplands and the soil pH ranges from 3.5 to 6.5. Therefore, a K_d of 1500 cm^3/g for loamy soil is selected for APG (Table 13) (Yu et al., 1993). But as discussed above, K_d can vary over many orders of magnitude depending on the soil type, pH, redox potential, presence of other ions, and soil organic content, which may bring significant uncertainty to the risk. This uncertainty is further discussed in the following section on analysis of the results.

4.4 Bioconcentration Factor (BCF)

As discussed in the exposure algorithm section, the contaminant body burdens for aquatic receptors depend exclusively on the BCF in the model. As a result, the BCF can influence the result significantly. The BCF as defined by Swanson et al. (1997) is the ratio of the chemical concentration in an aquatic organism to its concentration in water at equilibrium and is designed to reflect an aquatic organism's assimilation of pollutants. The bioavailability of the contaminant can vary as a function of the physical characteristics of the element, the aqueous phase composition, soil and/or sediment characteristics, and an organism's taxon, biochemistry, and lipid content (Hoffman, 1995; Weiss, 1999).

Organism biochemistry can influence the BCF as demonstrated by Walker et al. (1996). They found that organisms with calcareous skeletons, exoskeletons, or shells accumulated higher concentrations of lead and strontium than organisms without, because these metals follow similar chemical pathways as calcium. Additionally, methyl mercury, which is hydrophobic, has a much greater tendency to be bioaccumulated than inorganic mercury, because the organic form more readily accumulates in aquatic

organisms with higher lipid contents (Newman et al., 1991). Furthermore, water characteristics such as pH and organic content can have a direct effect on the solubility of metals; as the pH decreases cations become more soluble, and as a result more bioavailable (Lithner et al., 1995; Newman et al., 1991). Table 14 shows the BCF values applied for APG aquatic plants and animals in the case study.

Table 14 BCF (L/kg) for APG Aquatic Plants and Animals (PNNL, 1998; Jøregensen, 1991; ECOTOX, 2000)

Receptor	Ta, V	Mo[c]	Cr
Phytoplankton	620	20000	23000
Periphyton			16000
Water millfoil			16000
Mountain whitefish[a]	10[b]	1000	1000
White sturgeon[a]		1000	1000
Pacific lamprey (juvenile)[a]		1000	1000
Rainbow trout (adults)		1000	1000
Rainbow trout (eggs)		1300	1300
Rainbow trout (larvae)		1000	1000

[a] Rainbow trout was applied as surrogate
[b] Aquatic BCF value was estimated based on the empirical equation (Sample et al.,1996).
[c] For the BCF value of aquatic animals, Cr was applied as surrogate for Mo

For the three concerned metals in the case study, aquatic BCF data were only available for experiments conducted with chromium compounds on Rainbow trout, the value was also applied to other fish. No additional BCF data were available for any other inorganics of interest or fish species. Because chromium and molybdenum are within the

same group of the Periodic Table, they possess similar physicochemical properties (Clements et al., 1993). Therefore, chromium data were used as the surrogate species for molybdenum. For tantalum, vanadium surrogates have been used. The associated BCF values for other organisms were estimated based on the empirical equation derived by Sample et al. (1996) using the water solubility (K_{so} mg/L) (Appendix A).

4.5 Reference Values

The relative NOAEL and NOAEC data were identified from multiple sources for the terrestrial and aquatic receptors of the case study (Sample et al., 1996; Efroymson, 1997; PNNL, 1998; ECOTOX, 2000). In instances where data for a particular receptor were unavailable, surrogates were selected based on taxonomy, life style, and/or toxicological response similarity (PNNL, 1998). The surrogates selected in the case study are shown in Table 15a and applied to the model with the body conversion method as discussed in Chapter 3. The reference values for the case study are shown in Tables 16-19. The associated endpoints are shown in Table 15b.

Likewise, when chemical information is lacking, other surrogates are used. A literature survey revealed that neither NOAELs nor LOAELs have been established for any tantalum compounds. However, because vanadium and tantalum are within the same group of the Periodic Table, they possess similar physicochemical properties (Clements et al., 1993). Therefore, vanadium data were used as the surrogate species for tantalum in addressing any modeling endpoint gaps.

Table 15a Surrogates and Receptors for APG and YPG

Sites	Receptor	Surrogates[a]	Contaminants[b]
APG	Beaver	River otter	Cr_2O_3
	Indiana bat	Little brown bat	$CrK(SO_4)_2$, K_2CrO_4, Cr^{+6}, MoO_4, $MoNa_2O_4$,$NaVO_3$ VSO_4
		Black Duck	$CrK(SO_4)_2$
	Mallard, American kestrel, barred owl, bald eagle	Chicken	MoO_4
		Mallard duck	VSO_4
	Fern, rush, slender blue flag	General terrestrial pants (lettuce, oats, tomato)	$K_2Cr_2O_7$, Mo, V
	Periphyton, phytoplankton, water millfoil	Algea and phytoplankton	CrK_2O_7
		Dinoflagellate	Mo, V
	Mountain whitefish, pacific lamprey white sturgeon	Rainbow trout, Carp	CrO_3
		Fathead minnow,	MoO_3, V_2O_5
YPG	Black tailed rabbit	Cottontail rabbit	Cr_2O_3 , $CrK(SO_4)_2$, K_2CrO_4, Cr^{+6}, MoO_4, $MoNa_2O_4$,$NaVO_3$ VSO_4
	Cactus mouse	White-footed mouse	
	Kit fox	Red fox	
	Mexican spotted owl, loggerhead shrike, gamble's quail	Black Duck	$CrK(SO_4)_2$
		Chicken	MoO_4
		Mallard duck	VSO_4
	Creosote bush, foothill paloverde trees, saguaro cactus	General terrestrial pants (lettuce, oats, tomato)	$K_2Cr_2O_7$, Mo, V

[a] Sample et al., 1996, PNNL, 1998

[b] Vanadium applied as surrogates for tantalum

Table 15b Evaluated Endpoints of NOAEL (or NOAEC) (Sample et al., 1996)

Receptors	Chromium (K_2CrO_4, Cr^{+6})	Molybdenum ((MoO_4 and $MoNa_2O_4$)	Vanadium[a] (VSO_4 and $NaVO_3$)
Terrestrial Animal	Body weight and mortality	Reproduction	Reproduction, mortality, body weight, and blood chemistry
Terrestrial Plants	Plant growth or yield	Plant growth or yield	Plant growth or yield
Aquatic Receptors	Mortality	Mortality	Mortality

[a] Vanadium applied as a surrogate for tantalum

Table 16 Terrestrial Plant Receptors and NOECs (Efroymson, 1997)

Terrestrial Plant	Chromium[a] (VI) (mg/kg/day)	Molybdenum (mg/kg/day)	Vanadium[b] (mg/kg/day)
Fern	1.8	2.0	2.5
Rushes	6.8	2.0	2.5
Slender blue flag	7.4	2.0	2.5
Creosote bush	11.0	2.0	2.5
Foothill paloverde trees	31.0	2.0	2.5
Saguaro cactus	21.0	2.0	2.5

[a] Analyte tested was $K_2Cr_2O_7$
[b] Vanadium applied as a surrogate for tantalum

Table 17 Terrestrial Animal Receptors and NOAELs (Sample et al., 1996; PNNL, 1998)

Terrestrial Animal	Chromium (VI) (K_2CrO_4) (mg/kg/day)	Molybdenum (MoO_4 and $MoNa_2O_4$) (mg/kg/day)	Vanadium[a] (VSO_4 and $NaVO_3$) (mg/kg/day)
[b]Eastern garter snake	1.33E-01	3.53	1.14E+01
Lizards	1.33E-01	3.53	1.14E+01
Woodhouse's toad	1.33E-01	3.53	1.14E+01
Beaver	1.5	6E-02	8.9E-02
White-tailed deer	9.2E-01	4E-02	5.5E-02
Cactus mouse	6.55	2.8E-01	3.89E-01
White-footed mouse	6.55	2.8E-01	3.89E-01
Mallard	1.33E-01	3.53	1.14E+01
Bald eagle	1.33E-01	3.53	1.14E+01
American kestrel	1.33E-01	3.53	1.14E+01
Cottontail rabbit	2.41	1E-01	1.43E-01
Black-tailed jackrabbit	2.41	1E-01	1.43E-01
Indiana bat	8.57	3.7E-01	5.1E-01
Lesser long-nosed bat	8.57	3.7E-01	5.1E-01
Kit fox	1.73	7E-02	1.03E-01
Gambel's quail	1.33E-01	3.53	1.14E+01
Loggerhead shrike	1.33E-01	3.53	1.14E+01
Barred owl	1.33E-01	3.53	1.14E+01
Mexican spotted owl	1.33E-01	3.53	1.14E+01
Sonora whipsnake	1.33E-01	3.53	1.14E+01
Desert tortoises	1.33E-01	3.53	1.14E+01
Desert spiny Lizards	1.33E-01	3.53	1.14E+01

[a] Vanadium applied as a surrogate for tantalum.
[b] For reptiles and amphibians (eastern garter snake, lizards, woodhouse's toad, sonora whipsnake, desert tortoises and desert spiny Lizards), NOAELs are derived from LOAELs (PNNL, 1998).

Table 18 Aquatic Animal Receptors and NOAECs (ECOTOX, 2000)

Aquatic Animal	Chromium (VI) (CrO_3) (µg/L/day)	Molybdenum (MoO_3) (µg/L/day)	Vanadium (V_2O_5) (µg/L/day)	Tantalum[a] (µg/L/day)
Mountain whitefish	1.2	4.19E+03	1.13	1.13
Pacific lamprey, juvenile	1.2	4.19E+03	1.13	1.13
Rainbow trout: adult, eggs, larvae	1.2	4.87E+03	1.07	2.89E+01
White sturgeon (common, mirror, colored, carp)	6.53E+01	4.19E+03	1.13	1.13

[a] For Mountain whitefish, pacific lamprey and white sturgeon, vanadium was applied as a surrogate for tantalum; for rainbow trout, data available for Ta_2O_5

Table 19 Aquatic Plant Receptors and NOAECs (ECOTOX, 2000)

Aquatic Plant	Chromium[a] (VI) (µg/L/day)	Molybdenum[b] (µg/L/day)	Vanadium[b,c] (µg/L/day)
Periphyton	2.3	3.0E+01	1.2E+01
Phytoplankton	2.3	3.0E+01	1.2E+01
Water millfoil	2.3E+01	3.0E+01	1.2E+01

[a] Analyte tested was K_2CrO_7; surrogate aquatic plants are algae and phytoplankton
[b]Surrogate aquatic plant is Dinoflagellate
[c]Vanadium applied as a surrogate for Tantalum.

4.6 Results of Case Study

Risks to the receptors of APG and YPG are illustrated by Figures 34-36. Error bars are applied in the figures to address the uncertainty resulting from the variability of the distribution coefficient, K_d. As discussed earlier, this coefficient is a function of mineralogy, pH, redox potential, and the presence of competing ions and complexing ligands. In addition, applying this coefficient infers equilibrium, which is a grossly inaccurate assumption. One recommendation will be to include speciation and transport codes in the ERA model to improve depiction of mobility and bioavailability. In the case study, an uncertainty factor was applied to K_d and its influence on the risk characterization is illustrated by error bars. The following equation was defined for the uncertainty factor (Cheng, 1998):

$$F = 1 + \frac{\%}{100} \tag{4.2}$$

The 900% range used results in a factor of 10. The code runs three iterations applying the following guidelines:

- iteration one is application of the code with the original parameter value;
- iteration two repeats iteration one and then multiplies the selected parameter by the uncertainty factor; and
- iteration three again repeats the first iteration and then divides the parameter by the uncertainty factor.

As illustrated in Figures 34 and 35, for both YPG and APG terrestrial plants, overall risk posed by the metals followed the order of Mo>Cr (VI)>Ta (with vanadium as surrogate) (Table 20). A slightly high potential adverse risk exists from molybdenum exposure, while hexavalent chromium and tantalum posed minimal potential risk. These

results are attributed to the greater soil-to-plant transfer factor for molybdenum as compared to chromium and tantalum (with vanadium as surrogate); the greater transfer factor results in an increase in contaminant uptake in the plant. Subsequently, the risk increases for animals with a high vegetation diet.

For terrestrial animals at YPG and APG (Figures 34 and 35a), a moderately high and slight potential adverse risk exist for mammals from exposure to molybdenum; overall risk from chromium and tantalum (again with vanadium as surrogate) fall into the potential risk category (Table 20). Because of the greater risk to terrestrial plants, molybdenum poses the greatest risk to herbivores. However, for avian species, exposure from any of the metals results in the least risk category -- potential; nevertheless, hexavalent chromium exposure presents a greater potential risk than molybdenum, with tantalum resulting in the least. Similar results are observed for other animals except for the beaver at APG, which exhibited a significantly greater risk than other terrestrial animals. This result is most likely attributed to the beaver's foraging habits of high aquatic and terrestrial vegetation consumption (Figure 35b). According to the model output of the beaver's ADDs distribution, Figure 35b is plotted and it shows that among the five concerned exposure pathways for beaver, ingestion of aquatic and terrestrial plants contribute a significant part of the resulted risk.

In contrast to terrestrial plants at APG, because of the higher bioconcentration of hexavalent chromium to aquatic plants, it poses a greater risk to aquatic plants than molybdenum, with again tantalum exposure resulting in the least risk (Figure 36 and Table 20). As a result of Cr(VI) exposure, a moderately high potential adverse risk exists

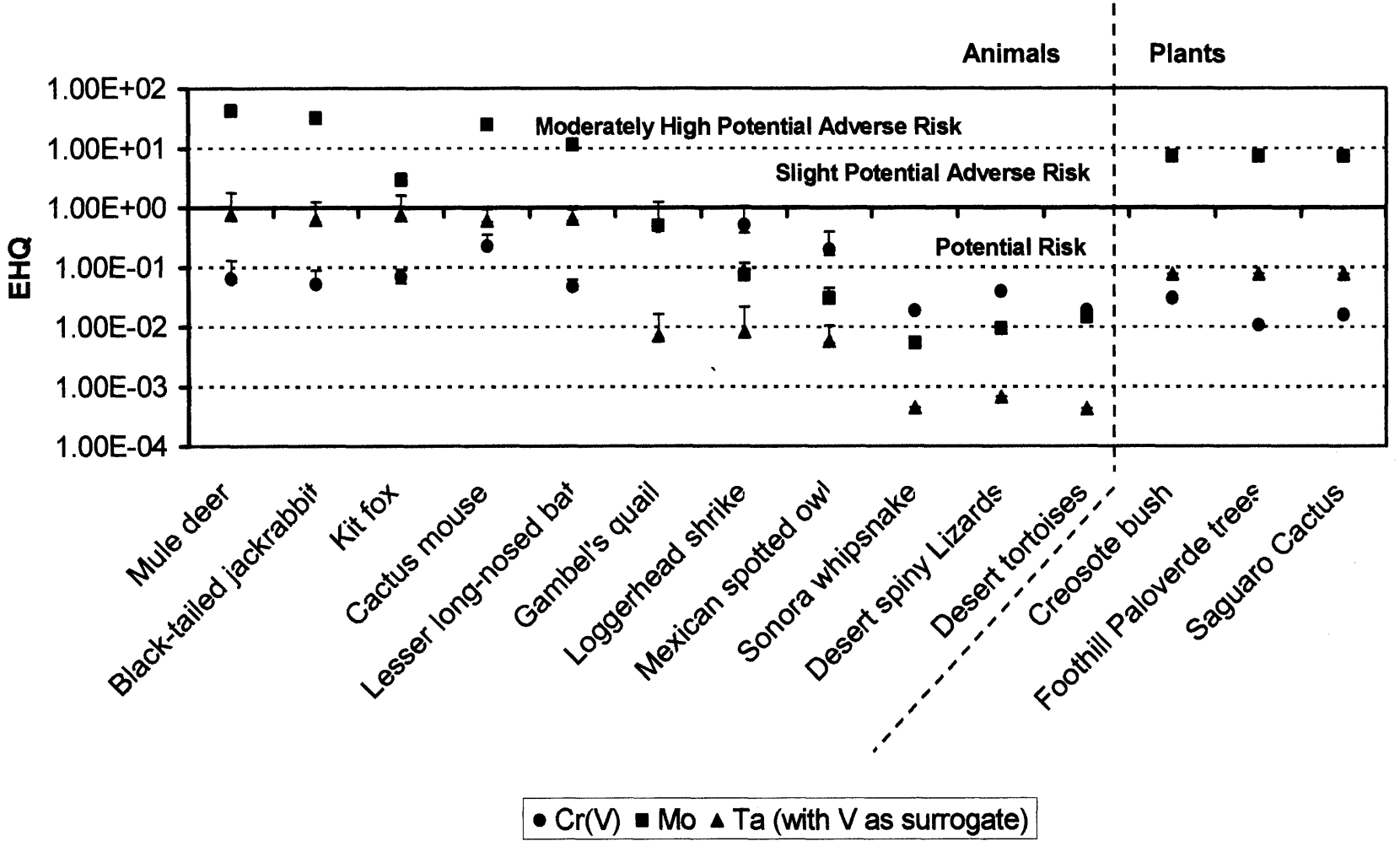

Figure 34 YPG Terrestrial Receptors EHQs (UF of 10 is applied to generate the error bars for Kd)

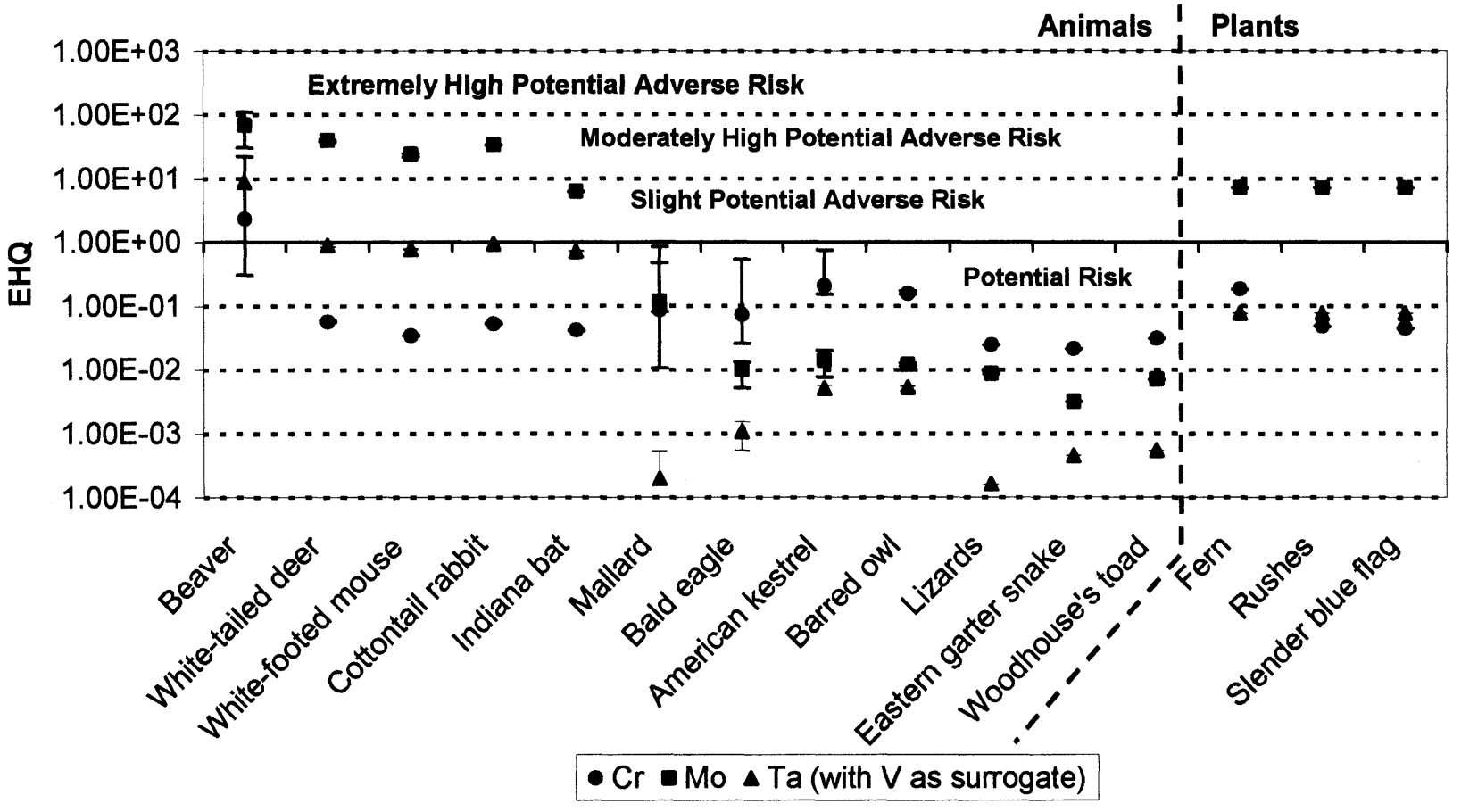

Figure 35a APG Terrestrial Receptors EHQs (UF of 10 is applied to generate the error bars for Kd)

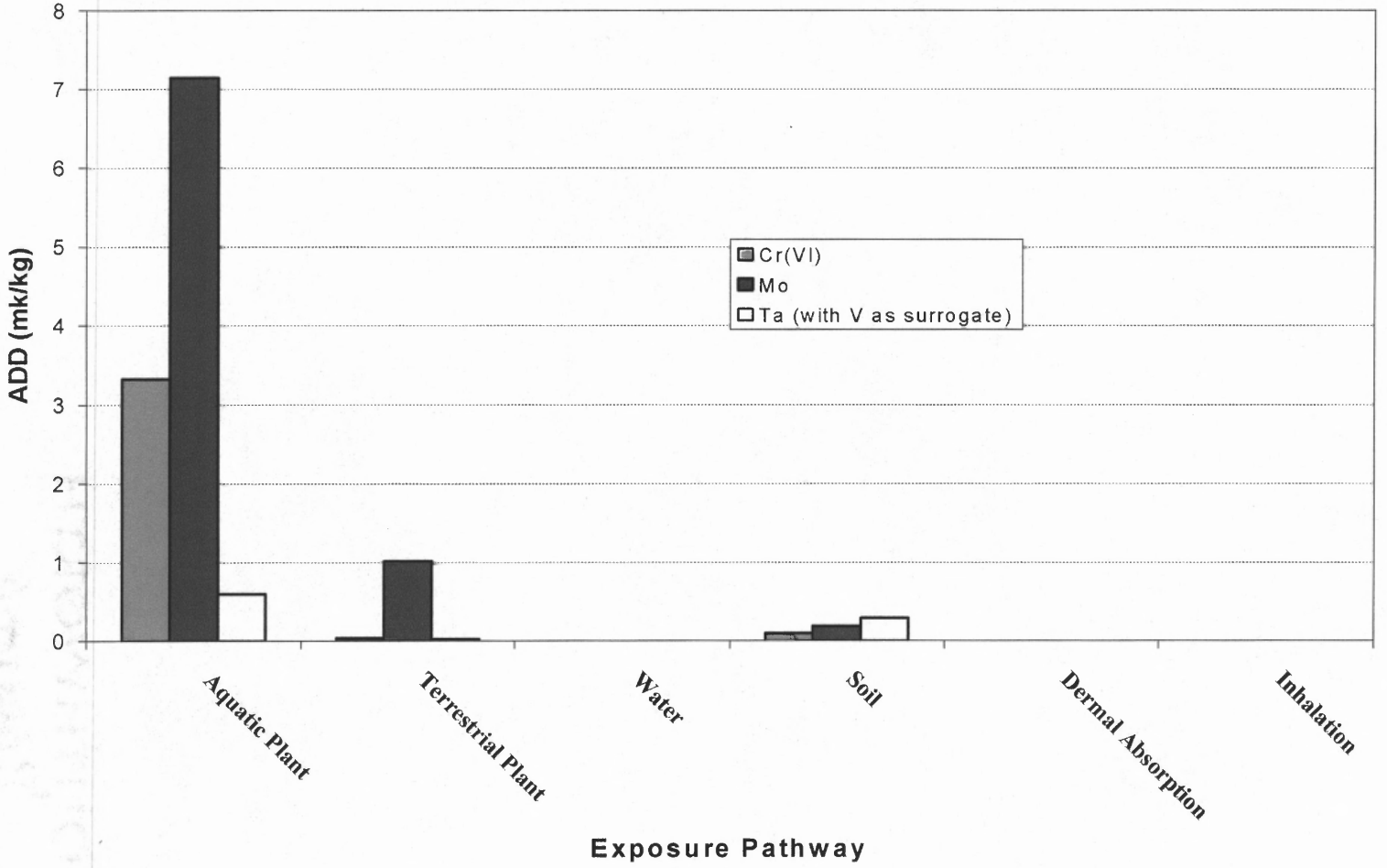

Figure 35b Beaver ADDs Distribution among Different Exposure Pathways (Ingestion of Aquatic and Terrestrial Plants and Animals, Ingestion of Water and Soil, Dermal Absorption and Inhalation)

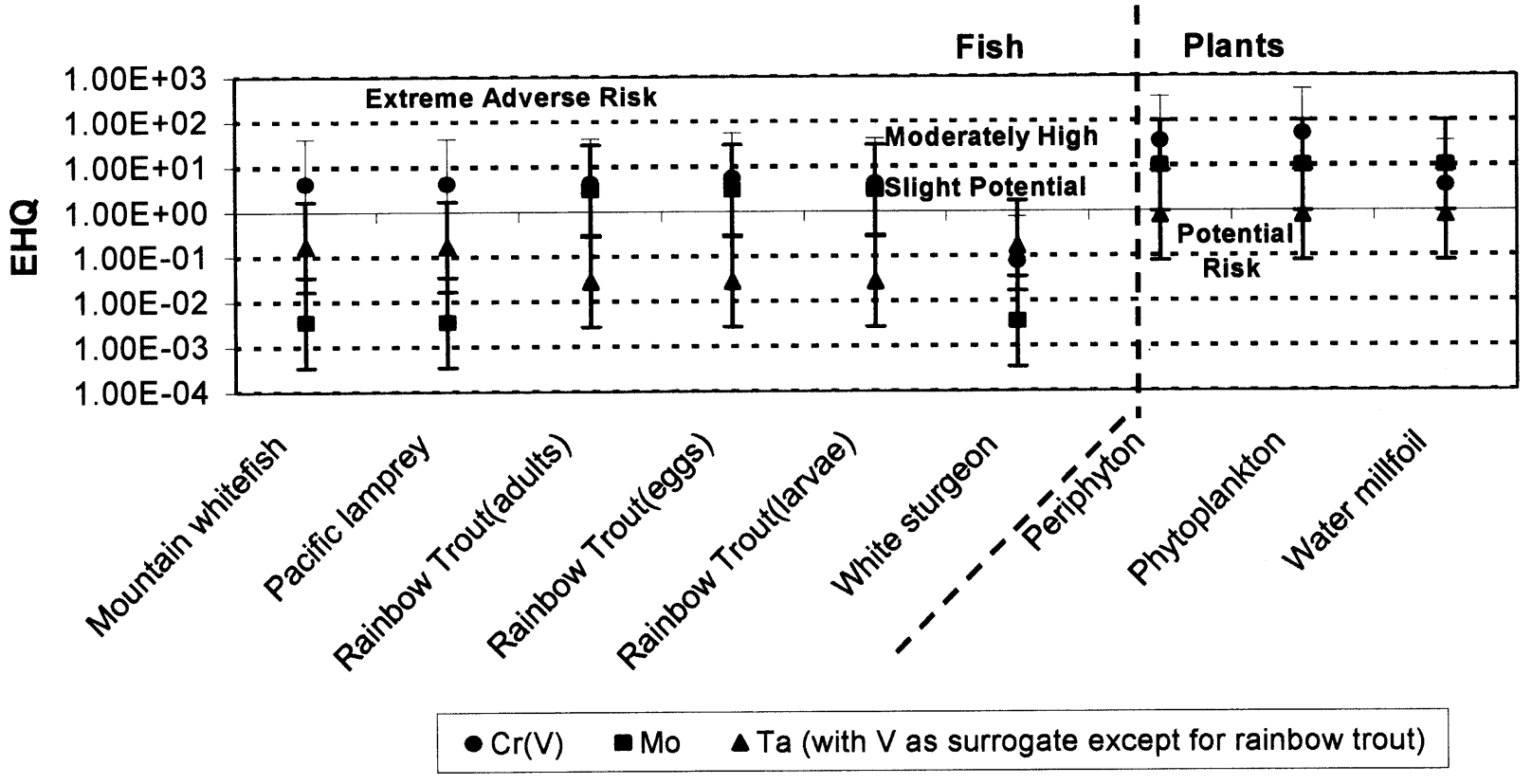

Figure 36 APG Aquatic Receptors EHQs (UF of 10 is applied to generate the error bars for Kd)

Table 20 Analysis of Case Study Results

	Receptors	Moderately high potential adverse risk	Slight potential adverse risk	Potential risk
YPG	Terrestrial Herbivores	Mo		Cr(VI), Ta
	Avian, Reptile & amphibian			Mo, Cr(VI), Ta
	Plants		Mo	Cr(VI), Ta
APG	Terrestrial Herbivores	Mo	Mo	Cr(VI), Ta
	Avian, Reptile & amphibian			Mo, Cr(VI), Ta
	Plants			Cr(VI), Ta
	Aquatic Animals	Cr(VI)	Cr(VI), Mo	Mo, Ta
	Plants		Mo, Cr(VI)	Ta

* All Ta data expect benchmark for rainbow trout are based on V surrogate

for periphyton and phytoplankton, and a slight potential adverse risk was observed for water millfoil. All the three aquatic plants are at a slight potential adverse risk from molybdenum exposure and a minimal potential risk from uptake of tantalum.

For APG aquatic animals, hexavalent chromium shows the greatest risk while tantalum poses the least. Chromium exposure results in a slight potential adverse risk to mountain whitefish, pacific lamprey, and rainbow trout (adults, eggs and larvae) and a potential risk to white sturgeon, while molybdenum poses a slight potential adverse risk to rainbow trout (adults, eggs and larvae), but potential risk to mountain whitefish, pacific

lamprey, and white sturgeon. Tantalum exposure resulted in a potential risk for all the studied aquatic animals. Compared to terrestrial animals, aquatic animals in APG are at significantly greater potential risk. This result may be attributed to their aqueous habitat, where they are continually in contact with the dissolved contaminant via direct absorption.

The different ranges of the error bars show how the variability of K_d influences the risk to the concerned receptors. Because of the coastal ecosystem, surface water is an important exposure pathway for receptors of APG. As a result from Figures 35 and 36, the change in K_d introduced great uncertainty to the risks posed to aquatic receptors and those for terrestrial animals which rely on aquatic species as their diet (e.g., beaver and mallard). In contrast, YPG has a typical desert environment where surface water is not an important exposure pathway for most receptors. As a result, the variability of K_d does not have as significant an effect on terrestrial animals as it did at APG, however, contaminated drinking water does impact the risk. Moreover, the applied UF can also affect the risks as different values are used.

Furthermore, selection of a proper surrogate is essential; if the surrogate is inappropriate it can be misleading. A surrogate should have similar physical and chemical characteristics so that when it is applied it can be expected to behave similarly to the contaminant of interest. However, a limitation is that even if a surrogate is closely related to the contaminant of concern, accuracy is nevertheless questionable. For example, based on toxicological studies, the LC_{50} for Ta was more than two orders of magnitude greater than that of V conducted on rats ingesting Ta_2O_5 vs. V_2O_5 (Gehartz,

1985; Lewis, 1996). Therefore, using vanadium as surrogates can overestimate the hazards associated with tantalum.

4.7 Uncertainty

As with any risk assessment, this ERA analysis has an uncertainty associated with it, which is attributable to the following factors:

1. Insufficient data on some model inputs such as BCF, necessitated assumptions that could not be tested. Since, where possible, conservative assumptions were made, this may possibly lead to overstatement of the potential risks to ecological receptors.
2. Insufficient data on exposure frequencies and synergistic effects from multiple stressors, resulting in a possible understatement of the risk to the receptors.
3. Employing surrogates for data not available with respect to certain receptors and chemicals may be questionable, misleading the ecological risk characterization process.

A comprehensive uncertainty analysis is currently being developed to address these factors and will be presented in the future.

4.8 Summary

Overall, as compared to hexavalent chromium and molybdenum, tantalum (with vanadium as surrogate) exposure presents the least risk (potential risk) to most of the receptors within APG and YPG. For all studies, a moderately high potential adverse risk exists for terrestrial plants exposure to molybdenum, while hexavalent chromium and

tantalum (with vanadium as surrogate) exposure resulted in a potential risk. The differences in these exposures can be attributed to the greater soil-to-plant transfer factor for molybdenum. As a result, the greatest risk occurred from molybdenum exposure to herbivores at both sites. Aquatic plants and animals exposure to hexavalent chromium resulted in a moderately potential adverse risk, which is significantly greater than exposure to tantalum (with vanadium as surrogate). The differences can be attributed to the hexavalent chromium BCF for aquatic receptors.

Considering that toxicity studies are conducted on a variety of species (Weiss, 1999), the resulting EHQ may not accurately represent true contaminant behavior; using surrogates, when data are not available, also introduces uncertainty into the risk characterization. In addition, applying soil-water distribution coefficients and bioconcentration factors can influence the risk significantly since there is great variability in these types of parameters. As a result, an uncertainty analysis will be included in the future.

CHAPTER 5

MODEL EVALUATION

5.1 Model Validation

Validating a model is a critical step in the development phase. Because of the extensive work at YPG, the modeling results have been compared to field studies as well as to other earlier modeling efforts (Table 21) (U.S. YPG, 1999).

Table 21 Cr Body Burden Concentrations for Selected Receptors of YPG

Receptors	Field study data[1] (mg/kg)	CSM [2](only ingestion of food and soil) (mg/kg)	ERA model (mg/kg) (range with error)
Small rodents (mouse or rabbits)	0.55	0.135894	0.224 (0.211- 0.354)
Kit fox	-	0.05204	0.0682 (0.0539 -0.0973)
Gambel's quail	-	0.35316	0.479 (0.412 -1.251)
Loggerhead shrike	-	0.24485	0.502 (0.374 -1.040)
Great-horned owl	-	0.04914	-
Mexican spotted owl	-	-	0.1956 (0.1591 - 0.3884)

[1] Field investigation conducted by the U. S. Army Center for Health Promotion and Preventive Medicine (USACPPM), 1999; 102.4% recovery is associated with the laboratory control sampling with EPA 200.7 method
[2] Conceptual Site Model developed by USACHPPM in September 1998

In the field study, the U. S. Army Center for Health Promotion and Preventive Medicine (USACHPPM) (U.S. YPG, 1999) collected ten rodents (i.e., pocket mice, kangroo rats, etc.) from two impact sites on the Kofa Range area. Chromium was detected in nine rodent samples with detection limit of 0.5 mg/kg. Vegetation sampling

was also conducted and no chromium was detected in any of these samples where the detection limit was 0.2 mg/kg (U.S. YPG, 1999). Compared to field data, the chromium body burdens for rodents were estimated to be lower through this model. However, it must be noted that the collected rodents may have lived within the impact area for an extended period. Through the life history of the receptors, the contaminant absorption, transportation, bioaccumulation, and excretion can be a very complicated process influenced by the variations of ecosystem conditions, contaminant characteristics, and receptor's physiological properties. In the ERA model, exposure parameters were derived based on the receptor's life history (i.e., absorption and depuration factors). However, the natural variations are difficult to reflect in any mathematical model where uncertainty and variability exist. Furthermore, the uncertainty associated with the sampling and laboratory studies cannot be neglected. In another risk assessment, the Conceptual Site Model developed by USACHPPM was used (U.S. YPG, 1999). In this model, only ingestion of soil and food was considered; therefore inhalation and dermal absorption were not included. As a result, the body burden for the evaluated rodents was even lower than the estimated ones in this research.

5.2 Model Evaluation

In the first phase of this research, a critical review and application of three ERA models, CHEMS-1, RESRAD-ECORISK and CRCIA, were conducted (Table 22). Developed by the University of Tennessee, CHEMS-1 model is used to rank and score contaminant toxicity and exposure potential, based exclusively on the toxicity data. However, due to multiple toxicity data sources and therefore uncertainty, many hazard values overlapped

in the case study. Therefore, CHEMS-1 is not effective in distinguishing contaminant exposure and risk as a scoring tool. Furthermore, this model is also limited where only two animals are used to assess ecosystem toxicity. Overall, CHEMS-1 is not recommended as a tool for ecological risk assessment. The other two models, RESRAD-ECORISK and CRCIA were developed for ecological risk assessment, and overall there are limitations associated their application (Weiss, 1999). The RESRAD-ECORISK model developed by Argonne National Laboratory (ANL) features a transport model and a sensitivity analysis for the site characteristic parameters. This model, however, is designed only for soil contamination by using five terrestrial animals where the databases are not modifiable, limiting the model application. Developed by PNNL, CRCIA is designed to address how exposure to organic, inorganic, and radiological contaminants can affect a coastal habitat. This ecological risk assessment included the most comprehensive ecosystem of the models evaluated. However, some limitations associated with the model development need to be addressed: it is not user friendly as a spreadsheet; there is no receptor and chemical database; it requires estimation of numerous exposure parameters, increasing the uncertainty; and, there is no sensitivity analysis to address the uncertainty.

In this research, the recommended features of RESRAD and CRCIA were combined and limitations were addressed. Specifically, as seen in Table 22, the model developed in this work includes algorithms for assessing potential risks to aquatic and terrestrial animal and plant receptors; expansion of the receptor and contaminant databases; a DBMS for housing receptor, contaminant, and benchmark data;

Table 22 Model Evaluation

Features	RESRAD	CRCIA	ERA Software
Application	Assess contaminated soil	Assess a coastal habitat	Assess site specific ecosystem with default arid or coastal environments
Target Receptors	Five terrestrial animals (Robin, mallard, rabbit, mouse, and deer)	Terrestrial and aquatic animals and plants from the coastal habitat	Terrestrial and aquatic animals and plants living in arid or coastal ecosystem, including the U.S. Army's most concerned species.
Exposure Pathways	Ingestion for terrestrial animals	Root uptake, particle deposition, and vapor transfer for terrestrial plants; ingestion, inhalation, and dermal absorption for terrestrial animals; and direct absorption for aquatic species	Root uptake, particle deposition, and vapor transfer for terrestrial plants; ingestion, inhalation, and dermal absorption for terrestrial animals; and direct absorption for aquatic species
Food Web	Simple food web for lower trophic levels	Specific food web relationship based on single receptor and one application limited to the studied site	General and effective food web expression within a relational database including higher trophic levels
Database	Non-modifiable, data are limited	Excel spreadsheet, no database	Modifiable database, physically linking to external databases
Interface	MS-DOS program, and reformatting of the reports required to view text and tables	Excel spreadsheet, not an integrated software package for general use	Windows-based interface, clear and user friendly; integrated with ERA code and database
Transport Model	Includes a fate and transport model to account for chemical mobility	No transport model linked	Currently no transport model linked
Data Quality	Include sensitivity analysis for site specific data	No uncertainty analysis to address the data quality	A comprehensive uncertainty analysis currently being developed for all the important parameters within this model

a relational database approach to express food web relationship within the DBMS; links to external DBMSs; and a Windows-based interface.

However, this model currently is still under development, as there are some potential limitations currently being addressed:

- First, data stored in the DBMS are not sufficient, and need to be amended as required by a user-specific application. Currently, the local DBMS is physically linked to two external databases (ECOTOX and RTECS). However, the system has not yet been developed to handle temporary and modified data from external sources.
- Second, before employing this model, users need to identify the contaminant concentrations in the concerned media, either real or estimated. To address this limitation, accurate depiction of contaminant distribution mechanisms need to be included in the model. As mentioned earlier, there are many problems in applying simplified descriptions of contaminant interactions like that of the distribution coefficient (Yu et al., 1993). Therefore, future efforts will include mechanistic models with thermodynamic and transport parameters. Furthermore, a comprehensive uncertainty analysis is needed to address data quality of other parameters or surrogates used in the model.
- Third, based on the case study, only direct absorption was considered for aquatic animals. As discussed in Chapter 3, exposure through ingestion may also exert considerable risk for certain receptors. As a result, the exposure algorithm may need to be refined to include bioaccumulation via ingestion once the associated data become available.

- Fourth, currently the assessment is static, and transient effects are not included. In the future, contaminant mobility and transport will be integrated into the software. Moreover, as discussed in Chapter 3, speciation can influence the contaminant uptake, and therefore the chemical toxicity to the receptor.
- Fifth, chemical distribution within the organism cannot be characterized and treated as a homogeneous volume. Furthermore, the changes in organism function resulting from the presence of the chemical are not included. This limitation cannot be resolved until associated data are available.
- Lastly, the risk characterization is based on the potential effect a release has on an ecosystem, and does not yet include a life-cycle evaluation.

5.3 Discussion

Ecological risk assessment remains a dynamic and evolving discipline. Innovative approaches are being studied to address the limitation associated with the endpoints application and extend the ERA applications by including such aspects as temperature and life-time exposure.

Dose-response data applied to ecological risk assessment usually comes from single-species toxicity tests measured in the lab. However, populations, communities, and ecosystems are generally the entities to be protected. One method to resolve this incongruity between individual-based data and the complex biological entities in ecological risk assessments is applying species-sensitivity distributions as studied by Newman et al. (2000). They used a bootstrap method to address the ambiguity of selecting a specific distribution and estimation of the approximate number of species, which are usually handled with simple lognormal model. The simplicity of this bootstrap

method made it easy to integrate into other ERA models. However, whether any species loss is acceptable is equivocal, using this method could discount the importance of maintaining dominant and keystone species, and the influence of species interaction if not properly applied.

The "single stressor-single endpoint" issue considered in a case study of the St. Croix National Scenic Riverway involved the application of fuzzy set theory (Wenger et al., 2000). Wenger et al. applied a stressor/value matrix, which enables the analyst to formulate ranking of ecosystem stressors by aggregating the ecosystem data. Results from the case study demonstrated this to be a useful tool for identifying the most important anthropogenic stressors affecting the current state of the ecosystem, which is beyond the "single stressor-single endpoint" paradigm. However, it also showed that when compared with mathematical models, this analytic methodology yields results with significant levels of uncertainty as it is influenced by the data availability.

Besides endpoints, weather and time effects on the exposure need to be addressed in ERAs. A model was developed to account for the pesticide effects on growing herbivorous arthropods as a function of temperature and time (Akkerhuis et al., 1999). Designed for the life time exposure of a marine mammal to hydrophobic contaminants, a pharmacokinetic model was developed to include the mass balance expressions for partitioning, transport, and transformation in various organs and blood (Hickie et al., 1999). However, these approaches currently are just utilized based on site-specific studies and the applications are therefore limited. Further studies of using these approaches are needed for combining them with ERA modeling.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

6.1 Conclusions

The ecorisk model algorithms apply potential exposure pathways and are written in VB with a Windows-based interface that is linked to the DBMS. Based on the developed model, a case study was implemented to assess the implications of replacing electroplated chromium with alternative coatings, tantalum and molybdenum. For the exposure estimate, Yuma and Aberdeen Proving Grounds were identified as baseline ecosystems, which involve an arid desert system and a coastal environment. As two important proving grounds for gun barrel testing, it is critical to assess potential risks resulting from the chromium contamination in the ecosystem (U.S. Army YPG, 1999). Selection of terrestrial and aquatic plant and animal receptors was based on the U.S. EPA Guidelines (U.S. EPA, 1998), and they are summarized in Chapter 2. In addition, based on the two sites, the U.S. Army's most concerned species have been included. Potential exposure pathways included in the software are ingestion, inhalation, and dermal absorption for terrestrial animals; root and foliar uptake for plants; and direct absorption for aquatic species.

To accomplish this ecological risk assessment, surrogate use was essential. For chemicals, a surrogate should not only have similar physical and chemical properties to the species of interest, but they should also behave alike. For receptors, surrogates were selected based on taxonomy, life style, and/or toxicological response similarity (PNNL, 1998).

Results from this case study show that as compared to hexavalent chromium and molybdenum, tantalum (with vanadium as surrogate) exposure presents the least risk (potential risk) to most receptors within APG and YPG. For all studied terrestrial plants in APG and YPG, a moderately high potential adverse risk exists from molybdenum exposure, while hexavalent chromium and tantalum (with vanadium as surrogate) exposure resulted in a potential risk. This difference is attributed to the greater soil-to-plant transfer factor of molybdenum as compared to Cr and Ta. Because of the increased exposure to plants, Mo posed the greatest risk to herbivores at both sites. As the Cr(VI) BCF is much greater than that for Ta (with vanadium as surrogate), aquatic plants and animals exposure resulted in moderately potential adverse risk, while Ta and Mo exposure resulted in potential risk. Through the risk characterization process, it is recognized that employing surrogates when chemical and toxicity data are lacking is questionable and may mislead the model result. As in the case of tantalum compounds, the use of vanadium may increase resulting EHQs. Therefore, an additional area of concern within ecological risk assessment is the use of surrogates and proper selection of ones similar in terms of properties as well as speciation.

According to the risk characterization results, conservative approaches are recommended when EHQs are greater than 1. Only Mo and Cr(VI) resulted in EHQs exceeding 1. As moderately adverse risk, the greatest, is observed in the studies, a potentially significant impact on terrestrial receptors population exists since reproductive and mortality endpoints are evaluated for Mo and Cr(VI) respectively. Such adverse effects can also bring potential risk to the human health through the food chain. Therefore, Using of molybdenum or chromium as a coating in gun barrels is not

recommended, and further study would be essential to address any affected area when either was used. Subsequently, investigative actions would be recommended to reduce the effects. For those species receiving a slight adverse risk, field investigations that include receptors sampling are recommended However, with a well-defined management system, other considerations have to be integrated with the risk characterization results to make and justify risk management decisions. These considerations should include existing background levels of contamination, available technologies, costs of alternative actions, and remedy selections (U.S. EPA, 1997).

This work only addresses the potential affect chromium and tantalum may have on an ecosystem as a result of test firing guns. While this study does not address the entire life-cycle effect on ecology, based on the conservative exposures considered, Ta does not appear to pose a threat to either ecosystem. On the other hand, in addressing an ERA for other replacements in "green manufacturing", future work should address ecological impact and risk during each phase of the life-cycle processes.

6.2 Recommendations for Future Work

Based on the case study and model evaluation, the following are recommended for improving the ERA software:

1. Modifying the local database and linking it to external databases (ECOTOX, RTECS) for data use.
2. Including uncertainty analysis to address data quality.
3. Linking the ecological risk model with speciation and transport models to account for time, location, and contaminant mobility and bioavailability.

4. Addressing portability of the current version, for example, client/server system.

Furthermore, combining the ecological risk assessment with a life-cycle approach will take into account the overall cradle-to-grave perspective for sustainable development. As such, the next phase of research will include collecting information related within the stressors' life cycle.

APPENDIX A

EXPOSURE MODEL AND PARAMETERS

The following description represents a compilation of exposure formulas that were primarily derived from U .S. EPA's wildlife exposure factors handbook (U .S. EPA, 1993). Each mathematical equation for exposure incorporates species-specific information on diet composition, body weight, home range, food and water ingestion rates, and incidental ingestion rates of environmental media, as available.

Terrestrial Plants

Root Uptake from Root-zone Soil to Roots

$C_{pr} = EC_{rzs} \times K_{ps1}$ (Hope, 1995)

Where:

C_{pr} = contaminant concentration in plant roots, mg/kg
EC_{rzs} = contaminant concentration in root-zone soil, mg/kg
K_{ps1} = plant-soil partition coefficient for root-zone soil to roots, mg/kg(soil)/mg/kg(roots)

Submodel:

$K_{ps1} = 270 \times K_{ow}^{-0.58}$ (McKone, 1993)

where:

K_{ow} = contaminant-specific octanol-water partition coefficient, mol/L(water)/mol/L(octanol)

Calibration:

K_{ow} lookup from MEPAS chemical database or estimate from the equations in Appendix B.

Root Uptake from Root-zone Soil Solution to Roots

$C_{pr} = EC_{sw} \times RCF$ (Hope, 1995)

Where:

EC_{sw} = contaminant concentration in surface water in contact with roots, mg/L
RCF = root concentration factor, L/kg

Submodel:

$RCF = 0.82 + 0.03 \times K_{ow}^{0.77}$ (Briggs et al., 1982; 1983)

Root Uptake from Root-zone Soil to Above-ground Plant Parts

$C_{pa} = EC_{rzs} \times (K_{ps2}, B_r, B_v)$ (Note that one or the other of the terms in brackets would be used depending on whether the contaminant was organic (K_{ps2}) or inorganic (B_r, B_v). Equation modified from Hope (1995))

where:

C_{pa} = Contaminant concentration in above-ground plant parts, mg/kg
K_{ps2} = plant-soil partition coefficient for root-zone soil to above-ground plant parts, mg/kg(soil)/mg/kg(above-ground plant)
Br = Bioconcentration factor for vegetative plant parts, mg/kg(soil)/mg/kg(vegetative plant)
B_v = Bioconcentration factor for nonvegetative plant parts, mg/kg(soil)/mg/kg(nonvegetative plant)

Submodel:

$K_{ps2} = 7.7 \times K_{ow}^{-0.58}$ (McKone, 1993)

Calibration:

Br, Bv lookup from U.S. Department of Energy (1996) and Base et al. (1984)

Foliar Uptake (vapor)

$C_{pa} = EC_{vap} \times K_{pa}$ (Hope, 1995)

where:

K_{pa} = plant-air partition coefficient for air to above-ground plant parts, m^3/kg

Submodel:

$$K_{pa} = [0.5 + (0.4 + 0.01K_{ow}) \times \frac{RT}{H}] \times 10^{-3}\ m^3/kg$$ (Reiderer, 1990)

R = universal gas constant, 8.314 Pa-m^3/mol/K
T = temperature, K
H = contaminant-specific Henry's law constant, Pa-m^3/mol

Foliar Uptake (particulates)

$C_{pa} = EC_{par} \times K_{pa}$ (Hope, 1995)

Terrestrial Animals

Direct Absorption from Dermal Exposure

$ADD_{dcs} = [(SA \times AF \times P_{cs} \times EC_s \times CF \times \alpha_d)/BW) \times \theta \times \psi$ (modified from U .S. EPA (1991))

$C_{dc} = ADD_{dc} / k_e$ (Hope, 1995)

where

ADD_{dc} = absorbed daily dose from dermal contact, mg/kg
C_{dc} = contaminant body burden in receptor from dermal contact, mg/kg
EC_s = contaminant concentration in soil, mg/kg
SA = surface area of ecological receptor, cm^2
AF = soil-to-skin adherence factor, mg/ cm^2
P_c = fraction of receptor surface area in contact with soil per day, d^{-1}
α_d = contaminant-specific dermal absorption factor, mg/kg (contaminant body burden) / mg/kg (absorbed daily dose)
k_e = contaminant-specific depuration rate, d^{-1}

BW = body weight of receptor, kg
CF = conversion factor, 1×10^{-6} kg/mg
θ = site use factor, (ratio of contaminant area to home range)
ψ = seasonality factor; (fraction of time per year receptor occurs at site)

Submodel:

Birds: $SA = 10 \times (BW \times 1000)^{0.667}$ (U.S. EPA, 1993)
Mammals: $SA = 12.3 \times (BW \times 1000)^{0.65}$ (U.S. EPA, 1993)
Woodhouse's toads: $SA = 0.953 \times (BW \times 1000)^{0.725}$ (U.S. EPA, 1993)
Lizards: $SA = 8.42 \times (BW \times 1000)^{0.694}$ (U.S. EPA, 1993-salamander applied to lizards)
Western aquatic garter snake: $= 2 \times \pi \times 1$ cm radius (1 cm + 106 cm length) (U.S. EPA, 1993 and Stebbins, 1985)
Terrestrial arthropods: 0.0002 cm^2 (PNNL, 1998)

Calibration:

α_d = See MEPAS chemical database and U. S. EPA (1995,;1989)
k_e = See CRCIA (PNNL,1995)
P_{cs} = mammal: 0.22, other vertebrates: 0.25, arthropods: 1 (Maughan, 1993)
BW = lookup for species using U. S. EPA (1993), Dunning (1993), Silva and Downing (1995), Nagy (1983)
θ= 1
ψ = 1 for all species except common snipe (0.33), bufflehead (0.5), Forster's tern (0.5), cliff swallow (0.5), and bald eagle (0.5) (Ennor, 1991).

Inhalation of Volatilized Contaminants

$ADD_{iv} = [(IR_i \times EC_{va})/BW] \times \theta \times \psi \times B_t$ (modified from Hope (1995))
$C_{iv} = ADD_{iv} \times (\alpha_v / k_e)$ (Hope, 1995)

where:

ADD_{iv} = applied daily dose from inhalation of volatilized contaminants, mg/kg
C_{iv} = contaminant body burden in receptor from vapor inhalation, mg/kg
IR_i = inhalation rate, m^3/day
B_t = fraction of day spent in burrow, hr/24hr
EC_{vap} = concentration of volatilized contaminant in air, mg/ m^3
α_v = inhalation absorption factor, mg/kg (contaminant body burden) / mg/kg (applied daily dose)

Submodel:

IR_i U.S.EPA (1993) and CRCIA (PNNL,1998):

Species	**IR_i**
Mammals	$2 \times 0.5458 \times BW^{0.80}$
Birds	$2 \times 0.4089 \times BW^{0.77}$
Woodhouse's toad	5.8×10^{-4}
Lizards and western aquatic garter snake	$0.00045 \times (BW \times 1000)^{0.8}$
Terrestrial arthropods	$0.00045 \times (BW \times 1000)^{0.8}$

Calibration:
α_v lookup from CRCIA (PNNL,1998) and Owen (1990)
IR_i lookup for species using U. S. EPA (1993) or estimate from submodel

Inhalation of Fugitive Dust

$ADD_{ip} = [IR_i \times EC_{par})/BW] \times \theta \times \psi$ (Hope, 1995)

$C_{ip} = ADD_{ip} \times (\alpha_p / k_e)$ (Hope, 1995)

where:

ADD_{iv} = applied daily dose from inhalation of volatilized contaminants, mg/kg
EC_{par} = concentration of particulated-bound contaminant in air, mg/ m^3
C_{iv} = contaminant body burden in receptor from particulate inhalation, mg/kg
α_p = particulate inhalation absorption factor, mg/kg (contaminant body burden) / mg/kg (applied daily dose)

Calibration:
α_p lookup from CRCIA (PNNL,1998) and Owen (1990)

Incidental Ingestion of Soil or Sediment

$ADD_{si} = (EC_s \times FS \times IR_f) / BW \times \theta \times \psi$ (modified from U. S. EPA (1993) using site use fractions as above)

where:

ADD_{si} = applied daily dose from incidental ingestion of soil or sediment, mg/kg,
EC_s = contaminant concentration in surficial soil or sediment, mg/kg
FS = mass fraction of soil or sediment in the diet, as percentage of diet on dry weight basis
IR_f = food ingestion rate on dry-weight basis, kg/day

Submodel:
IR_f (U .S. EPA, 1993)

Species	IR_f
Mammals	$= 0.235\ BW^{0.822}$
Birds	$= 0.0582\ BW^{0.651}$
Woodhouse's toad	$= 0.013(BW \times 1000)^{0.773}$
Lizards and western aquatic garter snake	$= 0.013(BW \times 1000)^{0.773}$

Calibration:
FS lookup for species using U. S. EPA (1993)
IR_f lookup for species using U. S. EPA (1993) or estimate from submodel

Ingestion of Water

$ADD_{wi} = EC_{dw} \times (IR_{dw}/BW) \times \theta \times \psi$ (modified from U .S. EPA (1993) using site use fractions as above)

where:

ADD_{wi} = applied daily dose from drinking water, mg/L-day

EC_{dw} = average contaminant concentration at drinking water supply, mg/L
IR_{dw} = ingestion rate of drinking water, mg/day

Submodel:
IR_{dw} (U .S. EPA, 1993)

Species	IR_{dw}
Mammals	$= 0.099 \times BW^{0.90}$
Birds	$= 0.059 \times BW^{0.67}$
Woodhouse's toad	0
Lizards and western aquatic garter snake	0
Terr. arthropods	0

Calibration:
IR_{dw} lookup for species using U .S. EPA (1993) or estimate from submodel

Ingestion of Food

$$ADD_{fi} = \sum_{k=1}^{m} (C_k \times FR_{fk} \times IR_f/BW) \times \theta \times \psi \qquad \text{(modified from Hope (1995))}$$

where:
ADD_{fi} = applied daily dose from ingestion of contaminated food, mg/kg
m = number of food items in the diet of the receptor species
C_k = contaminant concentration in the k^{th} food item, mg/kg
FR_{fk} = wet weight fraction of the k^{th} food item in receptor diet, kg (food)/kg (diet)

Submodel
$C_k = (ADD_{fi} + ADD_{wi} + ADD_{si}) \times (\alpha_{ing}/ k_e) + C_{other}$ (modified from Hope (1995))
where:
C_k = contaminant concentration in food item k resulting from all appropriate uptake pathways (ingestion, inhalation, dermal absorption and etc.), mg/kg
C_{other} = contaminant concentration in food item k resulting from exposure pathways other than ingestion (inhalation, dermal absorption, direct absorption, plant root uptake and etc.) mg/kg
α_{ing} = ingestion absorption factor, mg/kg (contaminant body burden) / mg/kg (applied daily dose)

Calibration:
FR_{fk} lookup for species using U .S. EPA (1993)
α_{ing} Lookup from Owen (1990) and MEPAS chemical database

Aquatic Species
Direct Contact
$C_{aq} = EC_{sw} \times BCF$
where:

C_{aq} = contaminant body burden in aquatic receptor, mg/kg
BCF = contaminant-specific bioconcentration factor, L/kg

Calibration:
BCF = lookup from MEPAS and ECOTOX databases

Values for inorganic contaminants (metal) may also be obtained from the literature (Maughan, 1993) and database (U.S. EPA, 2000) or estimated from empirical equation derived by Sample et al. (1996) using the water solubility (K_{so} mg/L) of a contaminant:

$$\text{Log BCF} = 2.791 - 0.564 \log K_{so}$$

APPENDIX B

OCTANOL/WATER PARTITION COEFFICIENT

This appendix shows the regression equation for the relation of aqueous solubility and octanol/water partition coefficient.

Regression Equation for the Estimation of S (Lyman et al, 1990)

Eq.No	Equation[a]	Units of S	No.[b]	r^2[c]	Chemical Classess Represented
1	$\log S = -1.37\log K_{ow} + 7.26$	μmol/L	41	0.903	Mixed classes;aromatics and chlorinated hydrocarbons well represented
2	$\log S = -0.922\log K_{ow} + 4.184$	mg/L	90	0.740	Mixed classes;pesticides well represented
3	$\log S = -1.49\log K_{ow} + 7.46$	μmol/L	34	0.970	Mixed classes; several pesticides
4	$\log 1/S = 1.113\log K_{ow} - 0.926$	mol/L[d]	41	0.935	Alcohols[e]
5	$\log 1/S = 1.229\log K_{ow} - 0.720$	mol/L[d]	13	0.960	Ketones[e]
6	$\log 1/S = 1.013\log K_{ow} - 0.520$	mol/L[d]	18	0.980	Esters[e]
7	$\log 1/S = 1.182\log K_{ow} - 0.935$	mol/L[d]	12	0.880	Ethers[e]
8	$\log 1/S = 1.221\log K_{ow} - 0.832$	mol/L[d]	20	0.861	Alkyl halides[e]
9	$\log 1/S = 1.294\log K_{ow} - 1.043$	mol/L[d]	7	0.908	Alkynes[e]
10	$\log 1/S = 1.294\log K_{ow} - 0.248$	mol/L[d]	12	0.970	Alkenes[e]
11	$\log 1/S = 0.996\log K_{ow} - 0.339$	mol/L[d]	16	0.951	Aromatics[e](benzene and benzene derivatives)
12	$\log 1/S = 1.237\log K_{ow} + 0.248$	mol/L[d]	16	0.908	Alkanes[e]
13	$\log 1/S = 1.214\log K_{ow} - 0.850$	mol/L[d]	140	0.912	All chemical represented by Eqs. 4-12 plus propionitrile[e]
14	$\log 1/S = 1.339\log K_{ow} - 0.978$	mol/L[d]	156	0.874	All chemicals represented by Eqs.4-12 plus propionitrile[e]
15	$\log S = -2.38\log K_{ow} + 12.90$	μmol/L	11	0.656	Phosphate esters
16[f]	$\log S = -0.9874\log K_{ow} - 0.0095t_m + 0.77178$	mol/L	35	0.990	Halobenzenes
17[f]	$\log S = -0.88\log K_{ow} - 0.01t_m - 0.012$	mol/L	32	0.979	Rigid aromatic hydrocarbons (polynuclear aromatics)
18	$\log S = -0.962\log K_{ow} + 6.50$	μmol/L	9	0.878	Halogenated 1- and 2-carbon hydrocarbon (8 with Cl, 1 with Br)

a. S = aqueous solubility; K_{ow} = octanol/water partition coefficient; t_m = melting point (^{0}C), $t_m \geq 25^0$C; N = number of carbon atoms in molecule.
b. No. = number of compounds in data set used to obtain equation.
c. r^2 = square of correlation coefficient
d. Actually, moles/ 1000 g of water (i.e., molar solubility). For most chemicals this is very close to the molar solubility (moles/liter of solution), and no correction need be applied.
e. All chemicals used were liquids. Values of K_{ow} for many of these chemicals were estimated.
f. If t_m is less than 25^{0}C, a value of 25^{0}C should be used for t_m in Eqs.16-17

APPENDIX C

EXPOSURE PARAMETERS IN DBMS

In this appendix, the terrestrial animals exposure parameters stored in the DBMS are displayed, which include surface area, body weight, inhalation rate, ingestion rate and P_{cs}. Similar ones are developed for terrestrial plants and aquatic receptors.

Terrestrial Animals Exposure Parameters Stored in the DBMS

Receptor	Site	Surface Area[1] (cm^2)	Body Weight[2] (kg)	Inhalation Rate[3] (m^3/day)	Water Ingestion Rate[4] (mg/day)	Food Ingestion Rate[5] (kg/day)	P_{cs}[6] (day^{-1})
Beaver	APG	7.56E+03	1.95E+01	1.18E+01	1.43E+00	2.70E+00	2.20E-01
White-tailed deer	APG	1.91E+04	8.09E+01	3.67E+01	5.16E+00	8.70E+00	2.20E-01
White-footed mouse	APG	9.23E+01	2.22E-02	5.19E-02	3.22E-03	1.03E-02	2.20E-01
Cottontail rabbit	APG	1.26E+03	1.24E+00	1.30E+00	1.20E-01	2.81E-01	2.20E-01
Indiana bat	APG	5.49E+01	1.00E-02	2.74E-02	1.57E-03	5.33E-03	2.20E-01
Barred owl	APG	1.23E+03	1.35E+00	1.03E+00	7.23E-02	7.09E-02	2.50E-01
American kestrel	APG	2.48E+02	1.23E-01	1.63E-01	1.45E-02	1.49E-02	2.50E-01
Mallard	APG	1.09E+03	1.13E+00	9.01E-01	6.42E-02	6.32E-02	2.50E-01
Bald eagle	APG	2.42E+03	3.75E+00	2.26E+00	1.43E-01	1.38E-01	2.50E-01
Lizards	APG	1.80E+01	3.00E-03	1.08E-03	0.00E+00	3.04E-02	2.50E-01
Eestern garter snake	APG	6.47E+02	6.00E-02	1.19E-02	0.00E+00	3.08E-01	2.50E-01
Black-tailed jackrabbit	YPG	1.78E+03	2.11E+00	1.99E+00	1.94E-01	4.35E-01	2.20E-01
Kit fox	YPG	1.86E+03	2.25E+00	2.09E+00	2.05E-01	4.58E-01	2.20E-01
Cactus mouse	YPG	9.23E+01	2.22E-02	5.19E-02	3.22E-03	1.03E-02	2.20E-01
lesser long-nosed bat	YPG	5.49E+01	1.00E-02	2.74E-02	1.57E-03	5.33E-03	2.20E-01
Gambel's quail	YPG	3.03E+02	1.66E-01	2.05E-01	1.77E-02	1.81E-02	2.50E-01
Loggerhead shrike	YPG	1.31E+02	4.74E-02	7.82E-02	7.65E-03	8.00E-03	2.50E-01
Mexican spotted owl	YPG	1.23E+03	1.35E+00	1.03E+00	7.23E-02	7.09E-02	2.50E-01
Sonora whipsnake	YPG	6.47E+02	6.00E-02	1.19E-02	0.00E+00	3.08E-01	2.50E-01
Desert spiny Lizards	YPG	1.80E+01	3.00E-03	1.08E-03	0.00E+00	3.04E-02	2.50E-01
Desert tortoises	YPG	5.38E+02	4.00E-01	5.43E-02	3.00E+00	6.34E+00	2.50E-01

References:

[1] PNNL, 1998; U.S. EPA, 1993; Stebbins, 1985

[2] U.S. Army YPG, 1999; Silva and Downing, 1995; U. S. EPA, 1993; Dunning, 1993; Nagy, 1983

[3] U.S. EPA, 1993

[4] U.S. EPA, 1993

[5] U.S. Army YPG, 1999; U.S. EPA, 1993

[6] U.S. Army YPG, 1999; Maughan, 1993

APPENDIX D

CONTAMINANTS SPECIATION AND DISTRIBUTION

In this appendix, the dominant distribution and speciation of contaminant for the case study is presented.

Dominant Distribution and Speciation of Contaminant

		Cr(VI)	Mo	Ta	V[1]
EC_s (mg/kg)		7.5	13.84	31.32	-
APG (pH ≅ 5.5)	**K_d (cm^3/g)**	1500	90	1200	-
	E_{sw}(μg/L)	5	150	26	7
	Speciation	$HCrO_4^-$	MoO_4^{2-}	$HTaO_3$	$VO_2(OH)_2^-$
YPG (pH ≅ 8.0)	**K_d (cm^3/g)**	70	10	220	-
	E_{sw}(μg /L)	107	1380	140	39
	Speciation	CrO_4^{2-}	MoO_4^{2-}	$HTaO_3$	$VO_3(OH)^{2-}$

[1]V is applied as surrogate for Ta where E_{sw} was converted directly.
*Reference: Baes and Mesmer, 1986; Betrabet et al., 1984

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